THE JOURNAL

—OF THE—

AMERICAN CHEMICAL SOCIETY.

VOLUME XIX.

1897.

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EDWARD HART, Editor,

J. H. LONG,

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540.5 A5
v. 19, pt. 1
850-1
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Published Monthly. Price, $5.00 per Annum

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

VOL. XIX.—NO. 1.

JANUARY, 1897.

EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE,
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EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.

Entered at the Post Office, Easton, Pa., as Second Class Matter.

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VOL. XIX. [JANUARY, 1897.] NO. 1.

THE JOURNAL

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AMERICAN CHEMICAL SOCIETY.

THE PROPORTIONS OF CHLORINE AND OF NITROGEN AS NITRIC ACID AND AS AMMONIA IN CERTAIN TROPICAL RAIN-WATERS.

BY J. B. HARRISON AND JOHN WILLIAMS.

Received November 1, 1896.

DURING the years 1880 to 1885 determinations of the quantity of nitrogen present in the forms of nitric acid and ammonia were, from time to time, made by one of us upon samples of rain water which had fallen in the island of Barbados, British West Indies, and in others of the West Indian Islands.

It was noticed that the proportions of combined nitrogen present in the rain waters in the forms of nitric acid and ammonia did not in any way support the received ideas that tropical rain-water contains considerably higher proportions of combined nitrogen than does that of temperate climates.

When a Botanic Station was started in the island of Barbados, at Dodd's Reformatory, steps were taken to systematically collect samples of rain-water, representative of the whole rainfall. The samples were collected by J. R. Bovell, Esq., F.C.S., F.L.S., the superintendent of the Botanic Station, and analyzed as soon as possible after collection by one of us (J. B. H.). This was continued from June, 1885, to February, 1890, soon after the analyst was transferred to British Guiana.

In the latter colony, in January, 1890, steps were taken to carry out a similar investigation and samples representative of the whole rainfall were collected at the Government Laboratory and at the Botanic Gardens in Georgetown. The results reported in this paper are those obtained in Barbados in latitude

13° 4′, north, and longitude 59° 37′ west, during a period of four years and nine months, ended in February, 1890, and in Georgetown, Demerara, in latitude 6° 49′ 24″ north, and longitude 58° 11′ 30″ west, from January, 1890, to June, 1896, a period of six and a half years.

The investigation has therefore extended over a period of eleven years—long enough, we think, to supply a fairly reliable record of the contents in combined nitrogen of the rain-waters in these low latitudes.

Both in Barbados and at the Government Laboratory in British Guiana, the rain has been invariably collected by means of large (eight to ten inch) glass funnels fitted with 100 mesh wire gauze sieves to prevent the entrance, into the collecting vessel, of leaves, insects, etc.

At the Botanic Gardens, British Guiana, at the commencement of the investigation there, the rain was collected in an eight-inch copper rain gauge, later in both this and in a glass funnel, and finally by means of the glass funnel only.

From the commencement of the experiments the methods of analysis used have been but slightly varied. The chlorine has been always determined by direct titration with centinormal silver nitrate solution, standardized in solutions of sodium chloride of approximately the same strength as the rain-waters to be examined, using 100 cc. of the rain-water at each estimation.

During the first four years, the ammoniacal nitrogen was determined directly on the water by means of Nessler's test; a quantity of the water was made very faintly acid with oxalic acid specially purified from all traces of ammonia and nitrates, divided into two portions, one of which was allowed to act for two or three days until reduction of the nitrates was complete, upon zinc copper couples prepared as directed by M. W. Williams,[1] the other being kept for the purpose of diluting the standard ammonia solution used for comparison in nesslerizing the water which had been exposed to the action of zinc copper couples. The errors thus fell on the nitric nitrogen, but as the proportions of this in the rainfall under consideration was, as a rule, much higher than that of the ammoniacal nitrogen, the amount of error introduced would be small.

Since the publication of Warrington's paper[2] the ammoniacal

[1] Trans. Chem. Soc., *1881*, 100.
[2] *J. Chem. Soc.*, 55, *1889*, 537.

and nitric nitrogen have been invariably determined by the method there given; 500 cc. of the rain-water are boiled rapidly in a Keene's revenue still with a little recently ignited magnesia, or with a very minute amount of chemically pure sodium hydroxide prepared from sodium, until 200 cc. have distilled over. In an aliquot part of the distillate the ammonia is determined by nesslerizing. The residue in the flask of the still is transferred to a wide-mouthed stoppered bottle containing copper zinc couples and kept closely stoppered at the temperature of the laboratory, 25° to 30° C., for four or five days. The water is afterwards distilled and the ammonia in the distillate, representing the nitrogen originally present as nitric acid, determined. Traces only of nitrites in a few instances have been detected in the rain-waters.

During this investigation 306 samples, representing the whole rainfall, have been examined.

Fortnightly and frequently weekly examinations were made of the rainfall during the first eight years of the experiments, but since 1893 monthly examinations only have been made of the mixed rain-water collected during the month.

BARBADOS RAIN.

The average compositions of the yearly rainfalls are shown in the following:

Years.	1885. Seven months.	1886.	1887.	1888.	1889.
Inches of rain	34.65	74.50	59.52	55.77	66.11
No. of samples analyzed	22	36	44	38	53
		Milligrams per liter at 27° C.			
Chlorine	7.755	7.604	8.417	8.473	7.923
Nitrogen as nitric acid	0.097	0.255	0.173	0.153	0.200
Nitrogen as ammonia	0.116	0.070	0.076	0.046	0.082
		Pounds per acre.			
Chlorine	60.850	128.300	113.450	107.010	118.611
Nitrogen as nitric acid	0.761	4.302	2.332	1.932	2.994
Nitrogen as ammonia	0.910	1.181	1.024	0.581	1.228

The average compositions of the monthly rainfalls and of the wet and dry seasons were as follows:

Months and seasons.	No. of years.	No. of samples analyzed	Average rainfall in inches	Mgms. per liter at 27° C.			Pounds per acre.		
				Chlorine.	Nitrogen as nitric acid.	Nitrogen as ammonia.	Chlorine.	Nitrogen as nitric acid.	Nitrogen as ammonia.
January..	4	14	2.94	14.171	0.160	0.074	9.435	0.106	0.049
February.	4	13	2.03	21.514	0.195	0.093	9.890	0.089	0.043
March ...	4	11	1.66	17.796	0.240	0.124	6.691	0.090	0.046
April	4	10	1.17	16.818	0.346	0.161	4.457	0.092	0.042
May	5	13	3.65	8.706	0.226	0.068	7.181	0.187	0.056
June	5	18	4.49	9.489	0.161	0.069	9.648	0.163	0.070
July	5	21	6.98	7.479	0.170	0.094	11.822	0.268	0.148
August...	5	21	10.12	6.388	0.155	0.091	14.640	0.355	0.208
Sept'mber	5	19	8.00	5.838	0.103	0.061	10.574	0.186	0.110
October ..	5	20	5.56	5.904	0.161	0.073	7.468	0.203	0.092
November	5	20	8.19	5.422	0.233	0.051	10.056	0.442	0.094
December	5	13	4.61	9.977	0.263	0.048	10.416	0.275	0.050
Wet season July to November.		101	38.85	6.197	0.164	0.074	54.520	1.443	0.651
Dry season December to June.		92	20.55	13.422	0.215	0.077	62.461	1.000	0.358

Wide variations occurred in both the chlorine and nitrogen contents of different rainfalls. The samples which were examined during the investigation which had the highest and lowest contents showed as follows:

	Mgms. per liter.	
	Highest.	Lowest.
Chlorine	47.042	2.476
Nitrogen as nitric acid	0.914	0.001
Nitrogen as ammonia	1.812	none

The average annual rainfall during these experiments was at the rate of 59.40 inches, having as average contents in milligrams per liter at 27° C., 8.699 of chlorine, 0.181 of nitrogen as nitric acid, and 0.075 of nitrogen as ammonia, and yielding to the soil 116.98 pounds of chlorine, 2.443 pounds of nitric nitrogen, and 1.009 pounds of ammoniacal nitrogen per acre. Of these approximately two-thirds of the ammoniacal nitrogen and three-fifths of the nitric nitrogen were contained in the rain which fell in the five months comprising the rainy season, during which period electrical atmospheric disturbances are common in Barbados.

In 1886, on August 16, an opportunity occurred for the collection and examination of samples of the rain which fell whilst a hurricane was raging to the north of the island. 9.14 inches were collected and were found to contain

	Mgms. per liter.
Chlorine	42.52
Nitrogen as nitric acid	0.329
Nitrogen as ammonia	0.057

The rain of this storm supplied 0.681 pounds of nitrogen as nitric acid per acre, or equal to twenty-eight per cent. of the average amount present in an ordinary year's rainfall.

BRITISH GUIANA RAIN.

The average compositions of the yearly rainfalls collected in this colony are shown in the following:

Years.	1890.	1891.	1892.	1893.	1894.	1895.	1896. Eight months.
Inches of rain	125.63	109.38	128.03	135.24	76.67	82.56	64.55
No. samples analyzed	39	26	24	12	12	12	8
			Mgms. per liter at 27° C.				
Chlorine	8.293	5.284	3.827	3.155	3.032	4.187	5.179
Nitrogen as nitric acid	0.090	0.128	0.035	0.066	0.036	0.237	0.082
Nitrogen as ammonia	0.075	0.034	0.043	0.068	0.045	0.065	0.078
			Pounds per acre.				
Chlorine	235.780	130.900	110.595	96.600	52.640	78.280	78.710
Nitrogen as nitric acid	2.559	3.171	1.015	2.022	0.625	4.431	1.199
Nitrogen as ammonia	2.135	0.842	1.247	2.083	0.781	1.215	1.141

The average compositions of the monthly rainfalls and of the wet and dry seasons were as follows:

Months and seasons.	No. of years.	No. of samples analyzed	Average rainfall in inches	Mgms. per liter at 27° C.			Pounds per acre.		
				Chlorine.	Nitrogen as nitric acid.	Nitrogen as ammonia.	Chlorine.	Nitrogen as nitric acid.	Nitrogen as ammonia.
January	7	11	13.21	6.174	0.097	0.030	18.469	0.290	0.090
February	7	13	10.19	6.417	0.102	0.060	14.808	0.235	0.138
March	7	13	7.26	5.043	0.063	0.100	8.291	0.103	0.164
April	7	14	8.05	6.197	0.087	0.094	11.297	0.158	0.171
May	7	12	12.29	5.595	0.086	0.062	15.572	0.239	0.173
June	7	13	12.93	3.278	0.104	0.033	9.598	0.304	0.096
July	7	12	10.96	3.076	0.116	0.038	7.634	0.288	0.094
August	7	12	6.81	3.399	0.089	0.111	5.242	0.137	0.171
Sept'mber	6	9	2.50	4.846	0.119	0.014	2.743	0.067	0.008
October	6	8	1.99	7.113	0.120	0.142	3.205	0.054	0.064
November	6	8	5.58	4.001	0.121	0.121	5.056	0.153	0.153
December	6	10	14.94	3.321	0.049	0.023	11.236	0.165	0.078
Wet seasons December to February. May to July.	71		74.52	4.313	0.090	0.039	72.784	1.519	0.658
Dry seasons March and April. August to November.	64		32.19	4.915	0.092	0.091	35.829	0.671	0.663

During the period over which the experiments have been

spread, the rainfall has been at an average rate of 106.71 inches per annum and has contained 4.494 mgms. of chlorine, 0.0915 mgm. of nitric nitrogen and 0.055 mgm. of ammoniacal nitrogen per liter at 27° C. This is equivalent to a yield of 108.613 pounds of chlorine, 2.190 pounds of nitric nitrogen, and 1.351 pounds of ammoniacal nitrogen per acre.

During this part of the investigation the highest recorded contents of chlorine was 16.10, the lowest 0.45 mgm. per liter. The highest contents of nitric nitrogen was 0.823 and of ammoniacal nitrogen 1.376 mgms. per liter; the lowest in both cases was none.

THE INFLUENCE OF THE COLLECTING VESSEL UPON THE APPARENT COMPOSITION OF THE RAIN.

At the commencement of the investigation in British Guiana, samples were collected in the grounds of the Government Laboratory by means of a glass funnel and at the Botanic Gardens by means of an eight-inch rain gauge. It was at once noticed that the rain collected in the metal gauge invariably contained the higher proportions of ammoniacal nitrogen and usually also of nitric nitrogen. In consequence a glass funnel was afterwards used at the Botanic Gardens being placed on the tower of the house some fifty feet above the ground. During the latter half of 1890 determinations were regularly made of the contents of nitric and ammoniacal nitrogen in the rain collected by the two receivers. The following gives in mgms. per liter at 27° C. the results obtained from June to December, 1890:

		Collected by glass funnel.		Collected by metal gauge.	
Month.	Inches of rain.	Nitrogen as nitric acid.	Nitrogen as ammonia.	Nitrogen as nitric acid.	Nitrogen as ammonia.
June.....	13.17	0.087	0.123	0.352	1.860
July.....	10.90	0.225	0.046	0.723	3.257
August....	5.71	0.075	0.270	0.486	4.000
September.	3.18	0.263	0.026	3.047	1.138.
October....	0.16	0.823	0.296	0.626	1.057
November.	2.97	0.214	0.091		
December.	9.47	0.049	0.015	0.330	0.178

The rainfall amounted to 45.56 inches in the six months and whilst the rain collected by the glass funnel contained an average of 0.125 mgm. per liter of nitric nitrogen and 0.092 of ammoniacal nitrogen that collected in the rain gauge contained 0.660

and 2.007 mgms. per liter of nitric and ammoniacal nitrogen respectively. Examinations of the rain collected in the rain gauge showed that it usually contained phosphoric acid and that the high content of nitrogen, which might have been considered as characteristic of tropical rain, was due to contamination of the receiving surface by birds. It was noticed that birds, in which this colony is peculiarly rich, constantly frequented and perched upon the copper gauge whilst they avoided the glass funnel, scared, probably, by the reflected rays of the sun.

To further examine into this matter, in 1892, determinations were made on the rains collected in a small copper rain gauge and by a glass funnel in the grounds of the Government Laboratory. These were placed side by side, about twelve inches apart, at about three feet above the ground so as to avoid splashing from the soil, as it was probably to nitrification induced by such splashing that the high content of nitric nitrogen noticed in the rain collected in the Botanic Garden's rain gauge was due. The following are the results in mgms. per liter, at 27° C., of the comparisons made during the months of July, August, and September, 1892:

		Collected by glass funnel.		Collected in metal gauge.	
		Nitrogen as		Nitrogen as	
Month.	Inches of rain.	nitric acid.	ammonia.	nitric acid.	ammonia.
July	11.40	0.051	0.063	0.037	0.229
August	8.05	0.053	0.222	0.049	0.652
September.	5.78	0.060	0.007	0.126	2.751

The rainfall of 25.24 inches contained 0.053 and 0.100 mgm. per liter, respectively, of nitric and ammoniacal nitrogen when collected by the glass funnel and 0.061 and 0.942, respectively, when collected in the copper gauge. Here, where there was but little chance of nitrification being induced by splashings from the earth, it is evident that the excess of nitrogen in the water collected by the copper rain gauge, was almost entirely in the form of ammonia. We are desirous of placing these observations on record, as they may to some extent explain the high nitrogen contents reported at times in the tropical rain-waters by other observers.

In our results, as far as used for the determination of the nitrogen present as nitric acid and ammonia we have, of course, only taken into consideration the figures obtained from the examinations of rain collected by means of glass funnels.

COMPARISON OF THE RESULTS OBTAINED IN BARBADOS AND BRITISH GUIANA WITH THOSE REPORTED FROM ELSEWHERE.

With an average annual rainfall in Barbados of 59.40 inches, the rain contained 0.101 mgm. per liter of nitrogen as nitric acid and 0.075 mgm. per liter of nitrogen as ammonia. The average amount of nitrogen in the two forms was therefore equal to 3.452 pounds per acre per annum.

With an average annual rainfall in British Guiana of 106.71 inches, the rain contained 0.0915 mgm. of nitrogen as nitric acid and 0.055 mgm. of nitrogen as ammonia per liter, at 27° C. Thus, the average amount of nitrogen in these two forms was equal to 3.541 pounds per acre per annum.

We may safely assume, therefore, that during the eleven years over which the investigation has extended, the nitrogen contents of the rainfall present as nitric acid and ammonia was approximately three and a half pounds per acre per annum in these two colonies situated in the tropics and in the direct course of the trade-winds.

The total amount of nitrogen present in the Rothamsted rain-water is given by Warrington,[1] at 3.74 pounds per acre per annum, a figure with which our results obtained by similar methods of analysis closely agree.

The Barbados rain-water contained approximately three-fourths of the nitrogen as nitric nitrogen; the British Guiana rain-water, two-thirds of the nitrogen as nitric nitrogen; while in the Rothamsted rain-water the nitric nitrogen was approximately only one-fourth of the whole.

Results obtained in New Zealand and at Tokio, in Japan, quoted by Warrington in his paper, show decidedly lower contents of nitrogen in these forms; and in both of these places the ammoniacal nitrogen is present in the rain water in far higher proportions to the nitric nitrogen than we have found here in the tropics. It is probable, therefore, that the rain-water of the tropics contains a higher proportion of its nitrogen present as nitric acid than does that of temperate climates.

As regards tropical rain, the only published results we are acquainted with are those of Müntz and Marcano,[2] on rain-waters

[1] *Loc. cit.*

[2] *Compt. rend.*, 108, 1062.

from Caracas, Venezuela, and from St. Denis, Reunion. In the former the mean proportion of nitric nitrogen was found to be 0.578 part per million, in the latter 0.69 part.

These results are far in excess of the quantities found by us, although, from time to time, instances have occurred to us in which the nitrogen present as nitric acid has approached or even exceeded these amounts.

Possibly, the results obtained by Müntz and Marcano were from rainfalls lower in quantity than those which occurred during our present investigation, whilst probably the composition of rain-water may be materially affected by the prevalence or not of the trade-winds.

Briefly our somewhat extended investigation leads to the conclusion that the rainfalls of certain tropical climates whilst containing a higher relative proportion of the nitrogen as nitric acid, do not supply to the soil a larger quantity of nitrogen as nitric acid and as ammonia than is supplied by the rain-water of temperate climates.

ANALYSIS OF AN IRON RAIL TAKEN FROM A GALLERY OF AN UNUSED COAL MINE.

By H. P. Talbot and A. G. Woodman.

Received November 21, 1896.

THE section of the rail in question was taken from a gallery of the "Hub Mine," at Glace Bay, Cape Breton. The gallery was allowed to fill with water in 1872, and was pumped out by the Dominion Coal Company last year. The rail had, therefore, lain unused in the gallery for over twenty years, most of the time under water which is reported to be "impregnated with acid," and, as indicated by the analysis, had undergone an entire change in composition. The rail was initially, presumably, of cast iron, and it is interesting to record the report which has come to us, that utensils of steel, and articles of wrought iron, did not undergo material change during the same length of exposure to the same conditions. So far, the writers have not had opportunity of examining any of these samples of wrought iron or steel.

After the mine had been pumped out, the rail was found to have lost its initial density and strength, and was easily broken or cut into fragments.

In the sample which came into our possession, there was a well-defined demarcation between the inner core, which was gray and very soft, and the outer shell, which was black and relatively hard, although this too could be readily cut with a knife and powdered in a mortar. The two portions were easily separated by running a knife blade along the line of demarcation. The outer and inner portions were examined separately.

Before presenting the results, the writers wish to state that the analytical work has been done at irregular intervals, and that the results are given solely for the interest which the figures seem to possess in themselves, and with the consciousness that, considered as an investigation, the report would be incomplete.[1]

The results are as follows:

	Outer shell.	Inner core.
Specific gravity (compared with water at about 20° C.)	2.45	2.16
	Per cent.	Per cent.
Lost on ignition at a red heat	7.50	8.75
Total iron	42.00	38.10
Total silicon	5.85	10.60
Total phosphorus	3.60	3.75
Sulphur evolved by treatment with acid	2.30	0.73
Sulphur in the residue after evolution method	2.35	0.68
Carbon corresponding to graphitic carbon	9.50	16.00

Manganese and aluminum were present in very small quantities. The former could not be precipitated in weighable quantities, except by using so large a sample that determination was not attempted.

No silicon, as such, was detected by ignition of the sample in dry chlorine. The presence of metallic iron was plainly indicated by the deposition of metallic copper, when fragments of the rail were placed in copper sulphate solution. The amount is distinctly larger in the outer shell than in the inner core. During solution in acids, a distinct odor of hydrocarbons was detected, but a combustion of the residue after treatment with copper potassium chloride, yielded a lower percentage of carbon

[1] Shortly after the transmission of the manuscript of this paper to the editor, a detailed description of the properties and analysis of other specimens from the same source, by F. W. Durkee, appeared in the *Am. Chem. J.*, **18**, 849. Interesting information concerning the mine-water, and the possible steps in the transformation of the iron, are also presented.

than was found in the residue after treatment with nitric acid (as given above). This may possibly be explained by the incomplete decomposition of the substance by the copper-ammonium salt, with the consequent protection of some of the carbonaceous by the mineral matter.

The loss on ignition at a red heat does not probably represent any definite quantity, but is given as having some possible interest.

The statement was made to us by one who had had opportunity to handle a fragment of the rail of considerable size, and during an interval of a year or more, that its density perceptibly increased with length of exposure to the air. The determinations of specific gravity already cited, were made about April 15, 1896. New determinations, made November 14, gave as results, for the outer shell 2.83, and for the inner core 2.23. While these results confirm the general statement, we do not feel that they are above criticism, as they were obtained from small fragments. They are comparable, however, with the earlier specific gravity determinations.

In connection with the foregoing statements, it is interesting to note the results reported by Herting,[1] of an analysis of a similar fragment of rail, which not improbably came from the same source, as he mentions it as coming from a mine in Cape Breton, in which the rail had remained for twenty years. His results are as follows:

Specific gravity, 2.053; silicon, 14.20 per cent.; graphitic carbon, 24.20 per cent.; phosphorus, 5.85 per cent.; total sulphur, 1.00 per cent.; manganese, 1.93 per cent.; iron, metallic, 31.50 per cent.

He finds that approximately one-half of the sulphur is volatile with acids, as in the results cited in this paper, and considers that the iron is otherwise present as Fe_3O_4. His percentages, upon recalculation, yielded the following: Ferrous sulphide, 1.37 per cent.; ferrous sulphate, 2.38 per cent.; manganese monoxide, 2.50 per cent.; phosphorus pentoxide, 13.37 per cent.; magnetic oxide (Fe_3O_4), 39.34 per cent., which with the carbon and silicon, yields a total of 97.36 per cent. It would appear, however, from our results, that the silicon was probably present as silica in his samples as well, at least in some measure.

[1] *Chem. Ztg.*, 20, 54.

Our analytical examination has not been, and cannot well be continued further than to afford the results cited above; hence we prefer not to express a positive opinion as to the probable combinations of the constituents as they occur in the rail, nor do we feel able to offer any explanation as to how the changes in composition have been brought about. Merely for comparison with Herting's results, we present our own, calculated upon the same basis, except that the silicon is calculated as oxide.

They are as follows:

	Outer shell. Per cent.	Inner core. Per cent.
Carbon	9.50	16.00
Silica	12.45	22.55
Phosphoric anhydride	8.25	8.60
Ferrous sulphide	6.30	2.00
Ferrous sulphate	11.15	3.20
Magnetic oxide (Fe_3O_4)	46.80	49.20

The writers wish to express their obligations to Mr. J. B. Dillingham, and Prof. W. H. Niles, through whose courtesy they came into possession of the fragment of the rail, and to whom they are indebted for information as to its history.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM, NO. 6.]

THE OXALATES OF ZIRCONIUM.

BY F. P. VENABLE AND CHARLES BASKERVILLE.

Received November 20, 1896.

THE text-books of chemistry make either very little or no reference to the oxalates of zirconium. Beyond an occasional reference to the oxalate or basic oxalate gotten by precipitating with oxalic acid or an oxalate, we can find little mention of these compounds. Behrens, in his microchemical work, speaks of an oxalate prepared as colorless pyramids by precipitating a solution of zirconium sulphate with potassium binoxalate, but no analyses are given, and the crystals could scarcely have been the pure oxalate. Paykull[1] speaks of double oxalates being prepared with the alkaline oxalates (1:2) and of his failure to prepare the neutral oxalate. His methods, and indeed full results, are unknown to us, as we did not have access to the original paper.

We may summarize the work which follows in the succeeding pages by saying that we found it possible to prepare the basic oxalates by precipitation. This was usually in the form of

[1] Ofv. af. Vet. Ak. Förhandl. ref. in *Ber. d. chem. Ges.*, 12, 1719.

$Zr(C_2O_4)_2.Zr(OH)_4$, though other ratios were gotten. The neutral oxalate we did not succeed in preparing, but instead the tendency seems to be toward the formation of the acid oxalate, $Zr(C_2O_4)_2.H_2C_2O_4.8H_2O$. This tendency toward the formation of acid salts was shown also in the double oxalates. Two of these were prepared. For sodium, $Zr(C_2O_4)_2.3Na_2C_2O_4.H_2C_2O_4.5H_2O$, and for potassium the salt $[Zr(C_2O_4)_2]_2.(K_2C_2O_4)_2.H_2C_2O_4.8H_2O$. The oxalate with ammonium as a constituent was not so easy of preparation in a pure state. The compound secured was $Zr(C_2O_4)_2.2(NH_4)_2C_2O_4$. The experiments and analyses are given in detail.

ZIRCONIUM OXALATES.

The Oxalate Gotten by Precipitation.—On the addition of a saturated solution of oxalic acid to a slightly acid solution of zirconium chloride until no further precipitation occurred, a gelatinous precipitate formed which had very nearly the composition $Zr(C_2O_4)_2.2Zr(OH)_4$. Analysis I gave Zr, 46.39, and C_2O_4, 30.89, instead of the theoretical 46.40 and 30.93 respectively. The filtrate from this was turbid, and on standing yielded another precipitate which had nearly the composition $2Zr(C_2O_4)_2.3Zr(OH)_4$.

These basic oxalates are very difficultly soluble in acids, and of extremely fine subdivision, settling slowly and passing through even the best filters. It does not seem probable that they could be secured of very constant composition. Probably basic oxalates with many different ratios between the oxalate and the hydroxide might be secured. On drying at 100°, or even a little lower, the oxalic acid is gradually volatilized and lost. This is true of all the oxalates and double oxalates prepared so that the only mode of drying these preparations was between filter paper.

The Acid Oxalate Prepared by Crystallization.—In preparing this oxalate, zirconium hydroxide was dissolved in oxalic acid. The hydroxide is quite soluble in oxalic acid, and a concentrated solution is readily obtained. A considerable excess of the acid is required to hold the oxalate thus formed in solution. If this solution be acidified by means of hydrochloric acid a very fine precipitate is obtained settling very slowly, easily passing through the best filter papers and insoluble even in a considera-

ble excess of the acid, but soluble in concentrated sulphuric acid. This precipitate was not analyzed, nor were the exact conditions of its formation determined, as its examination did not promise results of sufficient importance to justify overcoming the difficulties in the way.

On evaporating the acid solution of the oxalate the excess of oxalic acid first crystallized out. In the various preparations made, the first one or two crops of long crystals were found to be nearly pure oxalic acid, and were rejected. Then the form of the crystals changed to small granular or prismatic masses, and with each succeeding crop of crystals the percentage of zirconium increased, reaching speedily an approximately constant ratio. No difference in the form of the crystals in these different crops could be detected on superficial examination, and hence it was impossible to distinguish between the zirconium oxalate and the oxalic acid almost free of zirconium, except by analysis. In no case was the normal oxalate secured. The analyses showed a tendency toward the formation of an acid oxalate and to mixtures of this with the normal oxalate. These mixtures were gotten in the later crystallizations, but the last crystallization, when nearly the whole would solidify into a crystalline mass, showed decreased percentages of zirconium. It is possible that larger amounts than we had at our disposal would enable one to so fraction the crystallizations as to secure a pure oxalate. It is, however, questionable whether the normal oxalate can exist in solution without admixture with some oxalic acid.

Four series of crystallizations were made, and in two cases fairly abundant crops of crystals corresponding to the acid oxalate were obtained. In each series enough of the zirconium hydroxide was taken to form about twenty grams of the oxalate.

	First series. Sixth fraction. II.	Second series. Fifth fraction. III.	$Zr(C_2O_4)_2.H_2C_2O_4$.
Zr	25.44	25.28	25.53
C_2O_4	74.55	74.72	74.47

These are calculated upon the water-free basis. The crystals contained 29.34 and 29.27 per cent. of water respectively, where the salt $Zr(C_2O_4)_2.H_2C_2O_4.8H_2O$ contains 28.90 per cent. Other crops of crystals contained percentages of zirconium not varying greatly from these given above as 28.14, 27.62, 24.9, 23.83.

The percentage of zirconium in the normal oxalate is 33.96.

ZIRCONIUM SODIUM OXALATE.

The addition of sodium oxalate to a slightly acid solution of zirconium chloride gives a gelatinous white precipitate. Most of this dissolves in an excess of the oxalate. The undissolved portion settles to the bottom, and after prolonged standing, a second layer of a more powdery appearance forms. This can also be gotten by concentration of the filtrate from the first precipitate. Analysis showed that the first gelatinous precipitate was chiefly $Zr(OH)_4$. The second precipitate was a double oxalate of zirconium and sodium, but was either of inconstant composition (varying ratios of sodium to the zirconium), or was decomposed by the washing.

The analyses, calculated on a dry basis, gave:

	IV.	V.	VI.
Zr	53.12	46.86	41.98
Na	9.16	4.10	1.07
C_2O_4	38.06	39.64	42.95

If the solution made with the excess of sodium oxalate was diluted considerably with water, a gelatinous precipitate was formed, very fine and insoluble. Precipitates were also formed by the addition of hydrochloric acid. This mode of forming the double oxalate was abandoned, and the following method was adopted with greater success. Zirconium hydroxide was dissolved in an excess of oxalic acid, and to this a concentrated solution of sodium hydroxide was added, bringing it nearly to neutralization. When the solution was concentrated an abundant crop of crystals was obtained on cooling, a good deal of heat being evolved in the mixing. Further evaporation yielded other crops of crystals. These were washed, dried between filter paper and analyzed. The results are given in the following table:

	VII.	VIII.	IX.	Calculated.
Na	18.14	17.46	17.75	18.19
Zr	12.59	12.66	12.78	11.93
C_2O_4	69.27	66.89	69.47	69.88

These results show a somewhat wide variation from those calculated. This probably arises from the fact that the fractions were not composed of the crystals of a single kind of oxalate, but had other oxalates mixed with them in small amounts. Examined under a magnifying glass they seemed to be homo-

geneous, but the different crops could not be distinguished from one another. They were all small, hard prismatic crystals, somewhat difficultly soluble in water. One set of crystals, the analysis of which is reported under VII in the above table, was redissolved in water and recrystallized. On analysis it yielded the following results:

	VII.	XI.
Na	18.14	18.19
Zr	12.59	12.71
C_2O_4	69.27	69.10

These were calculated upon a water-free basis. The crystals from the various crops mentioned above did not contain a very constant amount of water, but ranged from 9.13 to 11.06. The calculated amount of water in $Zr(C_2O_4)_2.3Na_2C_2O_4.H_2C_2O_4.5H_2O$ is 10.62. It would seem, therefore, that the tendency, when this method of formation is adopted, is toward the formation of crystals containing free oxalic acid and with the sodium and zirconium oxalates bearing a ratio of three to one.

ZIRCONIUM POTASSIUM OXALATE.

The curdy precipitate gotten by precipitating zirconium chloride with normal potassium oxalate is insoluble in an excess of either of the substances. The precipitate first obtained is an impure zirconium hydroxide, containing only small amounts of oxalic acid. The supernatant liquid on concentration yields needle-like crystals of potassium oxalate, carrying only traces of zirconium. After the separation of a good deal of this potassium oxalate, further concentration yielded a gelatinous substance having the composition (XII): Zr, 39.34; K, 5.06; C_2O_4, 43.05; which seems to be a basic zirconium oxalate, mixed or united with a small proportion of potassium oxalate. If the potassium be calculated as potassium oxalate and subtracted, the composition of the remainder would be approximately $Zr(OH)_4.Zr(C_2O_4)_2$.

On adding potassium binoxalate to a solution of zirconium chloride a white curdy precipitate was obtained which was not completely soluble in excess of the binoxalate. The somewhat turbid solution was filtered and evaporated. Large crystals resembling those of oxalic acid formed. These were separated, and on analysis proved to be oxalic acid. At the same time a number of small crystals were formed, which were mechanically

separated, washed and dried. These were analyzed and are reported under XIII. A further crop was gotten from the mother liquor, and the analysis is given under XIV.

	XIII.	XIV.
Zr	19.59	17.99
K	16.18	13.91
C_2O_4	64.23	68.09

The curdy precipitate, which first formed, was also examined and found to have the composition $Zr(C_2O_4)_2.2Zr(OH)_4$.

The addition of a solution of potassium tetroxalate to zirconium chloride gave a gelatinous precipitate of zirconium oxalate (basic), carrying a little potassium oxalate. Subtracting the potassium oxalate, the percentages (XVI) Zr, 39.09 and C_2O_4, 38.63 are left, which are not very different from the figures gotten for the precipitate from potassium oxalate (neutral).

This curdy gelatinous precipitate was dissolved in excess of tetroxalate and the solution placed over sulphuric acid to crystallize, and yielded crystals having the composition (XVII): Zr, 20.85; K, 16.72; and C_2O_4, 62.31. As will be seen, these are not far from the 1 : 2 zirconium potassium oxalate, with excess of oxalic acid.

When potassium hydroxide was added to a solution of zirconium oxalate in oxalic acid until nearly neutral and then set aside for crystallization, various crops of crystals were gotten, as in the case of the double sodium oxalates. These crops of crystals were similar in appearance to the sodium crystals. They were analyzed and showed fairly constant composition.

	XVIII.	XIX.	XX.	XXI.	$(Zr(C_2O_4)_2)_2.$ $(K_2C_2O_4)_2.H_2C_2O_4.$
Zr	18.08	19.25	19.83	18.47	18.95
K	16.41	16.35	14.84	14.46	16.34
C_2O_4	66.51	64.40	65.33	67.07	64.71

The three previous analyses may also be referred to here as having approximately the same composition. See Analyses XIII, XIV, XVII. These are calculated as water-free. In the Analyses XVIII and XIX the percentages of water were 12.99 and 12.38. These would correspond to the formula $(Zr(C_2O_4)_2)_2.(K_2C_2O_4)_2.H_2C_2O_4.8H_2O$. In this case, as in the zirconium oxalates and the sodium oxalates, the crystals seem to form only along with free oxalic acid, giving acid salts.

ZIRCONIUM AMMONIUM OXALATES.

The addition of a solution of ammonium oxalate to the slightly acid solution of zirconium chloride gave a heavy gelatinous pre-

cipitate which was soluble in excess of ammonium oxalate and proved to be zirconium hydroxide with more or less zirconium oxalate and small amounts of ammonia. The filtrate from this precipitate was evaporated slowly and a fine crystalline powder obtained. This contained (XXII) Zr, 42.17 per cent. and C_2O_4, 39.86 per cent. This is in fair agreement with $Zr(C_2O_4)_2.Zr(OH)_4$. When ammonium oxalate is added until the first gelatinous precipitate is redissolved and then evaporated to crystallization, different crops of crystals can be gotten containing various amounts of ammonia. These did not seem to have any regular composition in our experiments and were looked upon as basic zirconium oxalates with varying amounts of ammonium oxalate present. Thus for one of these the figures (XVIII) Zr, 31.48; NH_3, 7.14; and C_2O_4, 61.38 were gotten.

Abandoning this method and using the one adopted in the cases of the sodium and potassium double oxalates, a more favorable result was obtained. Zirconium hydroxide was dissolved in excess of oxalic acid and then this was nearly neutralized by means of ammonium hydroxide. Analyses of these crops of crystals follow :

	XXIV.	XXV.	$Zr(C_2O_4)_2.$ $2(NH_4)_2C_2O_4.$
Zr	16.55	16.66	17.58
NH_3	14.46	13.35	13.28
C_2O_4	69.99	69.99	68.94

While these do not show that the crystals had been thoroughly purified, the results indicate that the composition is one zirconium oxalate to two ammonium oxalate. On recrystallizing one of these crops of crystals, zirconium hydroxide was observed to separate when the solution was heated (to evaporate to crystallization), and the crystals which were obtained consisted of ammonium oxalate alone.

In general it may be stated that the zirconium oxalate fails to show any decided tendency to enter into clearly defined combinations with the alkaline oxalates, exhibiting rather a power of crystallizing along with them in mixtures of any proportions. It can only be said at best that under the conditions of our experiments certain ratios seem to be preferred, and appeared more persistently. In all cases the crystals formed from oxalic acid solutions, and this free oxalic acid crystallized with them, giving acid oxalates.

UNIVERSITY OF NORTH CAROLINA, AUGUST, 1896.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 23.]

THE MECHANICAL ANALYSIS OF BASIC PHOSPHATIC SLAGS.

BY H. W. WILEY.

Received November 25, 1896.

BEFORE discussing the subject matter of the paper which I now present, I think it desirable to give a short sketch of the earlier literature relating to basic slags and the methods of their valuation.

In 1882, while examining some very finely ground bone in the Laboratory at Purdue University, Lafayette, Indiana, I noticed a marked solubility of the phosphoric acid therein in neutral citrate of ammonia. At that time Mr. H. A. Huston, who was a student in my laboratory, was directed to make some investigations of this phenomenon, and the results of his work were incorporated in his thesis for graduation, and the data were published in the proceedings of the Agricultural College of Indiana, Purdue University, for the year 1882.

In 1886 Jensch noticed that when lime and tricalcium phosphate were ignited together and the resulting mass pulverized, both citric acid and neutral ammonium citrate would extract phosphoric acid from the powder.[1]

In 1887, I published in Agricultural Science (March number) an article on the use of phosphorus contained in iron ores as a fertilizing material, after the conversion of the ores into iron or steel.

In 1889, I received from the Pottstown Steel Works a sample of phosphatic slag which was sent me under the name of cinder.

The superior merits of basic phosphatic slags as a fertilizer led me to believe that they might be largely soluble in neutral citrate solution. I therefore had this sample examined by Messrs. McElroy and Krug with that object in view. It was found to contain 20.20 per cent. total phosphoric acid, of which 12.25 per cent. were soluble in neutral ammonium citrate, the official solution used for the analysis of phosphatic fertilizers. An account of this property was published in the *Journal of Analytical Chemistry*, October, 1889. In this paper it is stated: "From the above results it is seen that in the phosphate slag we have a form of phosphoric acid equivalent in value to a first-class superphosphate."

[1] *Ber. d. chem. Ges.*, 19, 3093.

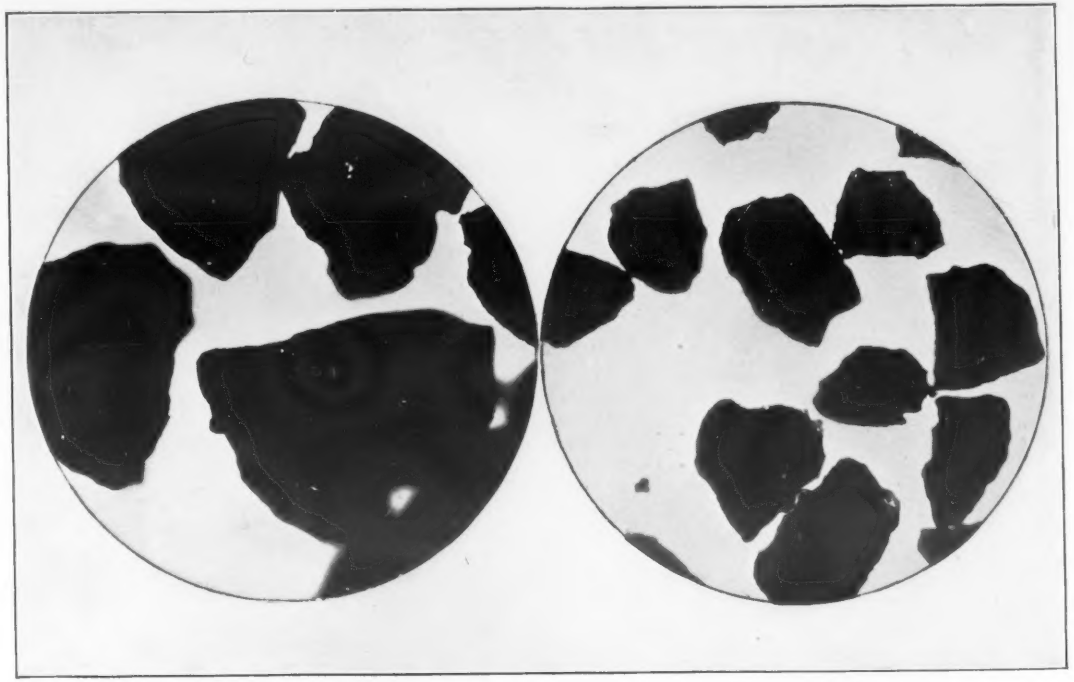
Petermann, in 1889, called attention to the fact that the calcium phosphatic limestone gives up phosphoric acid to a citrate solution.[1] In 1890 Jensch proposed the use of citric acid for the separation of tetra- from tri-calcium phosphate.[2] In 1892 Foerster published the statement that tetracalcium phosphate is easily soluble in ammonium citrate solution.[3]

Wagner proposed a special ammonium citrate solution having an excess of citric acid as a solvent for the tetracalcium phosphate in basic slags, and published an account of it in 1893.[4]

Since then the literature on this subject is very extensive, and it would be out of place here to attempt to cite the papers which have been published. It appears, from a study of the literature, that the first published account of the application of ammonium citrate as a method of valuing the availability of phosphatic slag was made from this laboratory in the paper published in the *Journal of Analytical Chemistry* above noted. For some reason, however, the method itself is universally known as the Wagner process.

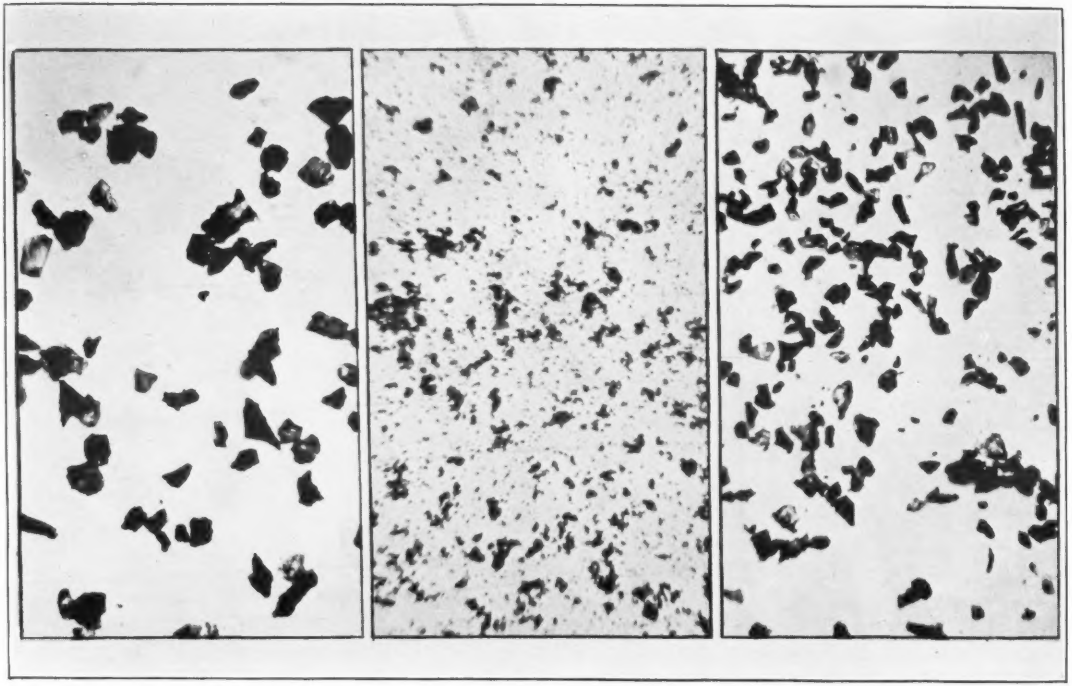
Experience has shown that the official method of determining available phosphoric acid, applicable to the reverted phosphoric acid in superphosphates, is of varying value when applied to phosphatic slags. The composition of phosphatic slags has been previously described by Krug and myself.[5] It is evident that the tetrabasic lime phosphate is less stable than the tricalcium phosphate and hence the phosphoric acid which it contains is more readily given up to the growing plant. When a basic phosphatic slag is treated with neutral ammonium citrate in the regular official manner, the quantity of phosphoric acid which passes into solution is, as a rule, far less than the available content of phosphoric acid as indicated by the effect of the fertilizer upon a growing crop. For this reason other methods of determining available phosphoric acid have been proposed and the one now in use is known as the Wagner process in which a strongly acid ammonium citrate solution is used as a solvent.[6] The method of solution employed is a purely arbitrary one but gives results generally comparable to the effects produced in the field.

[1] *Chem. Centrbl.*, 1889, **2**, 1036.
[2] *Ztschr. angew. Chem.*, 1890, p. 504.
[3] *Ztschr. angew. Chem.*, 1892, No. 113.
[4] *Chem. Ztg.*, **13**, 1153.
[5] *J. Anal. Appl. Chem.*, **5**, p. 685.
[6] Wiley's Agricultural Analysis, **2**, 80.



No. 1. ×60.
Greater than 0.25 millimeter in diameter.

No. 2. ×60.
From 0.10 to 0.25 millimeter in diameter.



No. 3. × 60.
Less than 0.10 millimeter in diameter.

No. 5. × 60.
Remaining suspended in alcohol for five minutes.

No. 4. × 60.
Remaining suspended in alcohol for two and one-half minutes.

The action of this solvent on phosphatic slags is very different for different samples. In some cases almost the whole of the sample is composed of pure tetracalcium phosphate and in these instances the solvent action of the reagent is very high. In other cases the sample may contain tricalcium phosphate, particles of silicious slags and also of iron and steel. In these instances, a low solvent action is noticed. It therefore has seemed desirable to supplement the chemical analysis of the slags with a mechanical separation. For particles of one-tenth of a millimeter in diameter and above, this separation is easily effected in a series of sieves, the finer sieves being made of bolting cloth. It is evident that a further separation of the fine particles cannot be secured with water, by reason of the action of this reagent upon the free lime which the slag contains.

About four years ago, I made some experiments looking to the substitution of alcohol in the place of water in the mechanical analysis of soils. The preliminary experiments succeeded so well that it was deemed advisable to use alcohol for securing the separation of the finer particles of the slag. The separations were made for me by Mr. C. C. Moore of the laboratory staff. The method of procedure is as follows: From twenty to fifty grams of the slag are placed in a shaking bottle and vigorously agitated for a few minutes on a milk-shake machine with ninety per cent. alcohol. This treatment serves to break up all the flocculates the sample may contain. The sample is placed in beakers entirely similar to those which are used in the mechanical separation of the soils by the subsidence method.

At first it was only desired to secue two series of separates of the fine particles and these were obtained by an arbitrary time of subsidence. All the particles which remained in suspension in a column of fifteen cm. of alcohol for five minutes were collected together and marked as separate No. 5. When all the particles which thus remained in suspension had been removed, another separation was made consisting of those particles remaining in suspension in like conditions, for two minutes and a half. This portion of the sample was collected and was designated as separate No. 4. The remaining portion of the sample was freed of alcohol and separated into three portions by sifting through two sieves made of bolting cloth with meshes of one-tenth and one-quarter of a millimeter diameter respect-

Less than 0.10 millimeter in diameter. Remaining suspended in alcohol for five minutes. Remaining suspended in alcohol for two and one-half minutes.

ively. All that portion passing through the one-tenth millimeter mesh is designated as separate No. 3. The portion passing the quarter millimeter mesh but not passing the tenth millimeter mesh is designated as separate No. 2. The portion not passing through the quarter millimeter mesh is designated as separate No. 1. The remarkably uniform size of these separates is shown by the accompanying photographs in which they are represented as magnified sixty diameters. By an inspection of separate No. 5, it is seen that it could be easily divided and another finer portion be secured, by means of a ten minutes subsidence in alcohol.

The alcohol used for the separation is of ninety per cent. strength.

The original sample and the separates were subjected to a chemical analysis, conducted for me by Mr. E. G. Runyan of the laboratory staff. The analytical work was confined to a determination of the total phosphoric acid and that soluble in the Wagner reagent. The data obtained follow:

	Original sample.	Separate No. 1.	Separate No. 2.	Separate No. 3.	Separate No. 4.	Separate No. 5.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total P_2O_5	16.54	13.91	16.14	16.71	18.21	18.16
Citrate soluble P_2O_5...	11.67	6.24	10.85	12.21	13.65	14.91
Proportion of original sample		12.00	33.00	26.00	8.00	21.00

From the above analyses, it is seen that the separates four and five contain not only the highest total quantity of phosphoric acid, but also the highest available acid. It is seen that there is a regular progression in the richness and availability of the sample from the coarsest to the finest parts. The relative proportions of the different separates to the whole are shown in the table. The data lead to the inference that it may be advantageous to the manufacturer of basic slags to secure at least a partial separation, in some such manner as indicated, for the purpose of being able to place on the market a more concentrated and available fertilizing material. The annual product of basic phosphate slags now amounts to about 1,500,000 tons and the output is rapidly increasing. Up to the present time American analysts have not had occasion to examine many samples of phosphatic slags but it is certain, in the near future, that the consumption of this material in the United States will rapidly increase. It is important, therefore, that investigations be made looking to the best methods of chemical and mechanical analysis.

PREPARATION OF SODIUM NITROPRUSSIDE.

By F. S. Hyde.

Received November 18, 1896.

THE literature referring to this compound is usually more or less incomplete in regard to the details of its preparation; but, unless it is prepared in the pure state, its use as a delicate reagent is somewhat impaired.

Place sixty grams pulverized potassium ferrocyanide in a medium-sized evaporating dish, and pour on it a solution consisting of 150 grams concentrated nitric acid (sp. gr. 1.42) diluted with 100 cc. of water. Perform the operation under a hood or in a draft of air. When the evolution of gases has ceased, evaporate on a water-bath with occasional stirring until a few drops of the liquid, mixed with water in a test-tube, no longer give a blue color with ferrous sulphate solution but, instead, a dark greenish cloud.

It may be necessary to continue the evaporation for an hour or more before the final test is obtained. However, the liquid which has a dark reddish brown color, should be evaporated to about one-half of its original bulk to insure success. Allow to cool slowly over night, when crystals of potassium nitrate, blackened with impurities separate out in stellated masses or needles.

Decant the liquid from the crystals (which are rejected) and neutralize it by stirring in dry sodium carbonate, producing a greenish brown froth and a red solution. This will require some patience on account of frothing; heat on the water-bath, filter and wash. Evaporate the red filtrate to one-half of its bulk or more, and allow it to crystallize by slow cooling on the water-bath.

The crystallization consists mostly of crusts of sodium and potassium nitrates, together with little red needles of nitroprusside. Pour off the mother liquor and treat the impure crystals with as little water as possible just enough to dissolve the nitrates and leave the red crystals. Then with this nitrate solution in the same dish, wash or "pan out" (with a rotary motion) the impurities from the crystals.

These red crystals may be recrystallized by dissolving in a small quantity of distilled water and evaporating the deep-red

solution in a beaker to small bulk, or better still until there is an incipient formation of crystals.

By slow cooling, as before, clusters of beautiful red rhombic needles are produced. Pour off the mother liquor and dry the crystals on filter paper.

The yield averages about twenty-five per cent. by weight of the ferrocyanide used. In one experiment, the writer obtained seventeen grams of the nitroprusside from sixty grams ferrocyanide, or over twenty-eight per cent. yield. Very little is gained by treating the mother liquors for an extra yield, especially in the case of small amounts.

Sodium nitroprusside ($Na_2Fe(NO)Cy_5 + 2H_2O$) has no melting point. When heated in a glass tube, the crystal gives off moisture and becomes black without disintegration. It is slowly soluble in cold water, but easily soluble in hot water. It is best known as a very delicate reagent for sulphur in the form of alkaline sulphides, producing violet colored solutions which gradually lose color on standing.

Certain organic compounds also react with sodium nitroprusside. For instance, with a weak aqueous solution of nitroprusside made slightly alkaline with caustic soda, formaldehyde gradually produces a dark amber tint; acetic aldehyde gives a blood-red color, becoming darker on standing, and finally violet after two or three hours; acetone produces a blood-red solution fading gradually to orange-red; and benzaldehyde gives no coloration.

IMPROVEMENTS IN THE COLORIMETRIC TEST FOR COPPER.

By George L. Heath.

Received November 9, 1896.

THE modifications of Heine's "blue test" described in some of the text-books[1] recently issued, admit of some improvement in speed of operation, ease of manipulation (in presence of the large amounts of iron, alumina and silica in poor slags or tailings), and finally in the making of the standard colors from solution of pure copper.

Having made a study of the process, and having had it in use

[1] Furman's Manual of Practical Assaying, *1895*, p. 159; Kerl's Metallurgy of Copper; Peter's Modern Copper Smelting, *1895*, p. 65.

several years at a large smelting works, modifications have been adopted which certainly present a few advantages, and a full description may be of interest to those who have occasion to use the test in technical work.

It is one of those tests where the principle is a very simple one, *i. e.*, the matching of colors of ammoniacal solutions of pure copper, but in which any improvement must be made in the small, but important, details of operation.

Copper has usually to be determined in tailings or lean blast furnace slags, and must be separated from silica, and oxides of iron, alumina, and lime.

The best conditions for effecting a complete separation have been made the subject of experiments detailed in this paper. The first authority quoted directs that "a standard of pure copper should be run with each set of assays, as the color fades on standing." That is true of standards made according to Furman's Manual, but it is possible to make color standards of ammoniacal solution of pure copper, which are very permanent, having been kept for a year without alteration. Stability of color may be secured if the following facts concerning the behavior of ammoniacal copper solutions be understood and applied.

It is easily proved that if ammonia be added to a very dilute solution of nitrate, or better, the sulphate of copper, until the basic salt redissolves in excess of alkali, the color produced is first purple, then purplish-blue, and finally with a large excess of ammonia, a clear and more permanent blue.

The blue color may then incline to greenish, if there is any organic matter in the reagents or substance analyzed, for a trace of organic matter in solution is apt to prevent the complete precipitation of ferric oxide by ammonia, and the trace yet dissolved, produces a greenish tint in the ammoniacal copper solution.

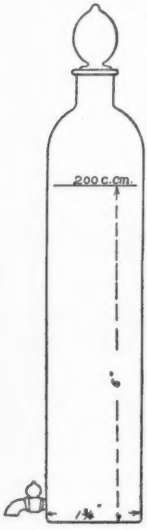
The color of standards for "blue tests" is found to be very permanent, (1) if the nitric acid used to dissolve the copper be replaced by sulphuric, (2) if the excess of ammonia be sufficient to produce the clear, neutral blue, and (3) if the color standards be kept in colorless glass bottles with very tightly fitting glass stoppers, preventing the slightest evaporation or loss of ammonia.

DIRECTIONS FOR PERMANENT STANDARDS.

Weigh a little over three-tenths gram of pure copper, place it in a flask or tall, narrow beaker, and dissolve it in five cc. of C. P. nitric acid (sp. gr. 1.40) and five cc. of sulphuric acid (sp. gr. 1.84). Evaporate carefully until the latter begins to evolve white fumes, and then cool, add twenty-five cc. of distilled water, and strong ammonia in sufficient excess to produce a clear solution again.

Prepare at least three liters of dilute ammonia (one volume to six parts by volume of distilled water) and dilute the copper with this until one cc. of the liquid contains exactly 0.0025 gram of pure copper, since two and a half grams of substance are always taken as a basis, and the degree of dilution then permits the whole range of colors to be made and diluted to a standard volume of 200 cc.

Measure accurately the portions of standard solution required for a set of colors, from 0.10 to 1.30 per cent. copper and make each one up to 200 cc. with the dilute ammonia. By this means a uniform tint and gradation of color is secured throughout the series.



The standards are kept in tall cylindrical bottles of thin, colorless glass, provided with accurately ground glass stoppers and having a mark on the side at 200 cc. They must be of strictly uniform thickness and diameter; the dimensions for a convenient size are shown in the sketch. (Extra bottles for the analyses might be provided with a stop-cock, as in a Hehner's colorimeter.) Screw the stoppers in very tightly, mix by shaking, and keep in a rather cool place, protected from direct sunlight.

With the exception of one bottle, whose stopper had become loose a few days ago, a set of such standards bottled January 1, 1896, do not differ from freshly prepared solutions of pure copper. (Refer to Experiments 1 and 2). The color of the one mentioned was remedied by filling to the mark with a few drops of strong ammonia.

ANALYSIS OF LEAN CUPRIFEROUS MATERIAL.

Crush and reduce the sample until the final portion, sufficient for analysis, will pass a one-hundred mesh sieve. If any pellets remain on the sieve, they should be weighed and determined separately.

It is considered better to take for analysis two and a half grams (or of material over one and two-tenths per cent., 1.25 grams) rather than one-half gram, as prescribed by some writers, since the decomposition is fully as rapid, and an occasional fine particle of metal, or difference in sampling, will introduce less error in the calculated percentage. If, however, only one-half gram should be taken, this test could be used with material containing nearly six per cent. copper. The method finds its best application between zero and two per cent.

Place the weighed sample in a No. 4 porcelain casserole four and a quarter inches in diameter at the top; barely moisten it with water to prevent caking, then add fifteen cc. of nitric acid (sp. gr. 1.42), and warm gently over a wire gauze until the covered dish is filled with red fumes, but not long enough to evaporate the acid. Remove, stir the mass, and break up any clots which may adhere to the dish.

When the decomposition appears to be complete, or all the copper dissolved, add five cc. of sulphuric acid (sp. gr. 1.84), place the covered casserole on a wire gauze or plate, and boil until the nitric acid is nearly driven off, and the mass has become a thick, but rather soft, paste. This insures the dehydration of the silica, and the change of copper to sulphate. From this point onward three practical modes of procedure are recognized, the choice of which depends on the judgment of the analyst, who may perform the following tests:

1. A working test, approximate, involving one precipitation of iron and alumina by ammonia and separation of the copper by filtration, and washing.

2. An accurate test, involving the previous separation of copper from the acid solution by reduction with aluminum. (See text-books.)

3. By the author's plan of a double precipitation by ammonia, which is sufficiently accurate and much more rapid than the second alternative plan, as will be evident from a later description.

I. To complete the working test, cool the residue in the casserole somewhat, add 120 cc. of water, washing the glass cover, stir well, heat until quite warm to the hand, and then add quickly enough ammonia (sp. gr. 0.9) to precipitate iron and alumina, and cause the liquid to smell very strongly.

Filter, with the aid of a pump, through a fifteen cm. German filter into one of the glass bottles, and wash the precipitate by repeated additions of dilute ammonia (1 : 10) until the bottle is filled to the mark, allowing each portion to run through before the next is added. When the mark is reached, allow ten cc. of washings to run into a tube placed against a white paper, and if no color is detected the washing is finished.

A thorough stirring of the precipitate with a rod after each addition of wash water is essential to the most complete extraction of copper. If the slag or tailings contain less than one per cent. of copper, the extraction is sufficiently complete for approximate working tests. (Refer to the appended table of experiments.)

In the presence of a large percentage, twenty-five per cent. or more, of oxides of iron and aluminum, the copper retained in the precipitate may be considerable, if the working is faulty, but will not generally run over 0.05 per cent. This error is, in the long run, pretty nearly balanced by the tendency to read the colors too high if the shade reaches to greenish-blue instead of blue. A purplish tint in the filtrate indicates, however, that sufficient ammonia was not added to effect the most complete separation of copper.

If this purplish tint in the blue is very pronounced an assay should be repeated, but if slight it may be remedied by the addition of ammonia, for which allowance is made by calculation in taking the color reading.

II. Accurate Method. The copper may be separated from the major part of the basic oxides by adding thirty cc. of water and five cc. of sulphuric acid to the decomposed slag in casserole, then adding a piece of aluminum (one inch square and one-sixteenth of an inch thick), and boiling gently till the copper is reduced.

Remove the aluminum to a beaker, filter the solution, and wash once. Then dissolve any particles of copper from the aluminum with hot dilute nitric acid (one part acid to two of water),

transfer as much as possible of the precipitate to the casserole, and pour the acid solution from the beaker through the filter, allowing the liquid to run into the casserole. After the copper is dissolved from the filter add three cc. of sulphuric acid, cover the casserole, and boil down with a moderate heat to remove nitric acid.

Finally, precipitate by ammonia, filter, and wash as usual. This, however, offers more chances for error, and is certainly less simple and rapid than the third alternative method proposed (that of double precipitation), as follows:

III. To the contents of the casserole, after boiling the material with nitric and sulphuric acids, add only seventy cc. of water, stir well to dissolve copper sulphate, then add rapidly an excess of ammonia (thirty cc. is generally sufficient), filter on a fifteen cm. filter, and wash twice with ten cc. of dilute ammonia (one part ammonia to ten of water). By means of a rod, and fifty cc. of water measured into a small wash bottle, transfer the precipitate as completely as possible to the casserole without damaging the paper. Add, drop by drop, enough sulphuric acid to just redissolve the iron or alumina, then follow with twenty to twenty-five cc. of ammonia (sp. gr. 0.9), or sufficient to precipitate the oxides again and cause the liquid to smell strongly. Filter and wash with dilute ammonia as usual. After stoppering and shaking the bottles the colors may be read within 0.03 per cent. by placing the bottle close to one of the standards against a window pane and placing a piece of perfectly white, unruled paper behind them.[1] Three bottles should never be placed closely together, as the middle one will appear too light.

A table of experiments is appended which shows the effects of variations in the working conditions. The battery assays are those of the same solutions whose color readings are given in the adjoining column, and since there are no impurities in the products tested to interfere with a battery assay, electrolysis furnishes an accurate estimation of the true amount of copper in solution and in the iron and aluminum precipitates which were dissolved in dilute sulphuric acid and electrolyzed. Most of the filtration, etc., was made by an assistant. A = Chemist, B = Assistant Chemist.

[1] Copper assaying on Lake Superior: *Eng. and Min. J.*, April 20, *1895*, p. 369.

No.	Remarks. Conditions of precipitation by ammonia, etc.	Per cent. oxides of iron and alumina.	Volume before precipitation. cc.	Shade of blue color after filtration.	Per cent. copper in ammoniacal solution. Color.	Per cent. copper in ammoniacal solution. Battery assay.	Copper in precipitate on filter.
1	Pure copper solution, standards unaltered.....	0	....	clear and neutral	0.80	0.80	0
2	" " " " "	0	....	" " "	1.20	1.20	0
3	[Method 1] warm solution precipitated quickly.	10 to 25	100	" " "	A 0.35 B 0.37	0.39	0.01
4	" " " " " "	10 to 25	100	" " "	A 0.29 B 0.29	0.31	0.01
5	" " " " " "	10 to 25	100	" " "	A 0.30 B 0.30	0.30	0.01
6	" " contains carbonaceous matter.....	25 to 35	100	greenish	A 1.32 B 1.34	1.29	0.07
7	" " warm solution, carbonaceous matter	25 to 35	100	very greenish	A 1.05 B 1.05	0.97?	0.05
8	" " warm solution, precipitated quickly	25 to 35	100	good, neutral	A 0.87 B 0.88	0.84	0.09
9	" " " " " "	25 to 35	100	" "	A 0.84 B 0.83	0.81	0.03
10	" " trace coke or charcoal in this sample	25 to 35	100	very greenish	A 0.79 B 0.75	0.71	0.08
11	" " ammonia added, drop by drop.....	25 to 35	100	good blue	0.88	....	0.08
12	" " " " quickly.....	25 to 35	100	" "	0.78	....	0.03
13	" " " " " warm as usual.....	25 to 35	130	" "	A 0.75 B 0.78	0.79	0.05
14	" " ammonia added slowly.....	25 to 35	130	" "	A 0.85 B 0.84	0.84	0.05
15 a	" " " " quickly.....	25 to 35	130	purple	A 0.86 B 0.88	0.88	0.11
15 b	" " " " " at boiling temperature	25 to 35	130	very purple	not read	0.93	0.06
15 c	" " boiled dry in casserole, precipitate warm	25 to 35	130	neutral	A 0.80 B 0.91	0.93	0.09
15 d	" 3 re-solution of residue and reprecipitation	25 to 35	1st time 70 2d time 50	"	not washed enough A 0.91 B 0.92	0.90	0.04
16 a	" 1 ammonia added, drop by drop, warm.....	25 to 35	130	purplish	A 0.69 B 0.69	0.70	0.10
16 b	" " ammonia added quickly, warm	25 to 35	130	nearly neutral blue	A 0.69 B 0.69	0.66	0.05
16 c	" " " " " "	25 to 35	130	very purplish	A 0.67 B 0.67	0.65	0.07
16 d	" 3 re-solution of residue and reprecipitation.....	25 to 35	1st time 60 2d time 50	nearly neutral	A 0.70 B 0.70	0.67	0.00

In the experiments with the approximate working test, the colors were read without any attempt to dilute to an exact match with the next lower standard, but the difference between the assay and the next lower and higher bottles was estimated by the eye, which, with practice, can be done within 0.03 per cent.

The tests marked "purplish" were not read until the shade (or tint) was corrected to that of the standards by the addition of a few cc. of ammonia.

If the first residue be boiled too dry, or the color be very purple after filtration, it will generally prove that the separation of copper from basic oxides by one precipitation with ammonia is very incomplete.

If the color be greenish there is a general tendency to read the colors a little too high, but the difference is generally slight and entirely within the limits of error in sampling. If the greenish tint be very pronounced the assay should be repeated, and if the trouble be due to the cupriferous material, the portion weighed for analysis should be kept for several minutes in a porcelain crucible at a full red heat and stirred with a platinum wire.

The writer recommends the general methods here given, in preference to those already in print, for reasons which have been specified, and considers modification No. 3 a better technical method than any one involving reduction of copper by aluminum for the following reasons:

a. A second precipitation of oxides of iron and aluminum will remove all but a trace of copper, if the washing be carefully completed, even when the material is rich in basic oxides.

b. No extra time is required for the second precipitation, since this dispenses with part of the necessary washing.

c. There is always a possible danger of incomplete reduction of copper by aluminum or of retention by the silica of a little copper (which would be extracted by ammonia), and more time is required, especially if the silica be removed by filtration before reduction with aluminum.

ON THE DETERMINATION OF STEARIC ACID IN FATS.

By Otto Hehner and C. A. Mitchell.

Received December 7, 1896.

THE quantitative determination of the individuals composing the mixture of fatty acids obtainable from any fat or oil is one of the most difficult problems of analytical chemistry and one which is very far from solved at the present time. Apart from the determination of certain constants, such as the iodine absorption, amount of potassium hydroxide consumed, etc., little more can be done than a rough separation of saturated from unsaturated fatty acids. A quantitative separation of the unsaturated fatty acids has barely been attempted, if we except the determination of the amount of hexabromide obtainable from the mixed fatty acids of linseed and other drying oils, measuring the linoleic acid, to which one of us referred at a recent meeting of the Society of Public Analysts, and concerning which we hope to publish the results of our joint work at an early date. The few figures published by Hazura, based upon the proportions of hydroxy acids obtained by the action of potassium permanganate upon unsaturated fatty acids, are obviously very rough and of no practical value.

For the separation of the solid fatty acids no quantitative method of any kind exists and here again inferences based upon the determination of physical constants and of the equivalents of mixtures have been the only available means. If it be known that a mixture contains two saturated fatty acids only and no more, the determination of the melting point or of the molecular equivalent is a satisfactory way of arriving at their relative proportions. But unfortunately there is no practicable method of proving that two and only two acids are present and, hence, all determinations hitherto made must be accepted with a considerable amount of doubt.

Heintz's well-known method supplies the only means of obtaining an insight into the qualitative composition of a mixture of non-volatile fatty acids, and Liebig's analogous method a means of examining a mixture of volatile fatty acids. Heintz's method is, however, solely a qualitative one and appears unsuited for analytical purposes. Without frequent repetition of the fractional precipitation nothing like a perfect separation of two closely allied fatty acids can be obtained. As, however, we

could find but few data on this point in the literature, we thought it advisable to ascertain to what extent Heintz's method was capable of concentrating the fatty acid of higher molecular weight from a mixture of known composition, by a single precipitation only.

FRACTIONAL PRECIPITATION.

Stearic Acid.—A considerable quantity of fatty acids obtained in the usual manner from cocoa-butter was dissolved in as little hot alcohol as possible, and when cold, the crystallized mass was pressed in a linen cloth. The residue was again dissolved in hot alcohol and the residue again pressed. After repeating this crystallization ten times the melting-point remained constant at 68.5° C. (Heintz gives 69° C. as the melting-point of stearic acid), and had a molecular weight of 283, as determined by the amount of potassium hydroxide consumed and the percentage of barium in the barium salt. (Theory for stearic acid, 284.)

Palmitic Acid.—In most of our experiments we made use of pure palmitic acid obtained from palm oil and prepared by Hopkin and Williams. This melted at 61.8° C. (Heintz, 62° C.), and had a molecular weight of 255.5 (theory 256). Subsequently we prepared palmitic acid from Japan wax. To the experiments made with the latter we shall refer later on.

Precipitation with Barium Acetate.—A solution of barium acetate was prepared containing 8.94 grams of barium acetate in 100 cc. of water, of which solution five cc. contained 0.241 gram barium, capable of combining with one gram of stearic acid. The mixed fatty acids were dissolved in 100 cc. of hot (methylated) alcohol of ninety-eight per cent., and the required quantity of barium acetate solution was added drop by drop from a burette to the hot alcoholic fatty acid solution, which was shaken after the addition of every drop. After cooling the precipitates were filtered off, thoroughly washed with cold alcohol of ninety-eight per cent., dried in the water-bath, and the barium contained in them determined by ignition with sulphuric acid. From the amount of barium sulphate obtained the molecular equivalent of the precipitated fatty acids was calculated and from this the amount of stearic acid by the formula:

$x = \frac{284(m-256)}{m(284-256)}$ where x is the required amount of stearic acid, m the molecular equivalent found, and 284 and 256 the equivalents of stearic and palmitic acids, respectively.

The filtrate and washings from the first precipitate were mixed and a second fraction of the fatty acids remaining in solution precipitated with barium acetate solution and treated as before. In some cases a third and fourth precipitation was made. The results are given in the following table:

I.

Stearic acid.	Palmitic acid.	Barium acetate solution added.	Barium salt.	Containing barium.	Molecular weight of fatty acids.	Stearic acid in precipitate.	Weight of recovered stearic acid.
Grams.		cc.	Grams.			Per cent.	
1	1	5	(1) 0.9614	0.1919	275.5	71.7	0.549
		5	(2) 0.4326	0.09	261.75	22.2	0.076
		5	(3) Too small for accurate estimation.				
							0.625
1	2	5	(1) 1.0046	0.2021	272.9	62.8	0.5039
		5	(2) 0.9696	0.1985	273	63	0.4983
		5	(3) 0.5122	0.1066	261.6	22.3	0.0904
							1.0926
1	3	5	(1) 0.8830	0.1827	263.2	27.9	0.1953
		5	(2) 0.9100	0.1863	267.3	42.8	0.3097
							0.5050
1	3	5	(1) 0.8920	0.1842	264.4	30.9	0.2187
		5	(2) 1.0315	0.2125	265.2	35	0.2866
							0.5035
0.5	0.5	2.5	(1) 0.5376	0.1082	272.8	62.7	0.2692
1	1	2.5	(1) 0.5246	0.107	268.3	46.6	0.1946
			(2) 0.5262	0.1065	270.4	54	0.2266
							0.4212

As a further means of getting some idea of the composition of the precipitated fractions, we recovered the fatty acids by shaking the barium salts with ether and hydrochloric acid in a separating funnel, washing the ethereal solution several times with water, evaporating the ether, and determining the melting-point of the mixed fatty acids. We thought it well to check,

on this occasion, the table of melting-points constructed by Heintz, referring to mixtures of stearic and palmitic acids. The following are our results, in comparison with Heintz's.

II.

Stearic acid. Per cent.	Palmitic acid. Per cent.	Heintz[1] M. P. °C.	Hehner and Mitchell. °C.
100	0	69.2	68.5
90	10	67.2	66.5
80	20	65.3	64.2
70	30	62.9	61.5
60	40	60.3	59.4
50	50	56.6	55.6
40	60	56.3	55.5
32.5	67.5	55.2	54.5
30	70	55.1	54.2
20	80	57.5	56.5
10	90	60.1	59.0
0	100	62.0	61.8

It will at once be seen, by a glance at these tables, that any judgment as to the composition of a mixture of stearic and palmitic acids based on the melting-point can only be very roughly approximate, especially when the acids are present in about equal proportions, there being only about 1.5° C. difference between mixtures containing fifty and thirty per cent. of stearic acid. Still, it enabled us to some extent, to confirm the results given in the first table, obtained by determining the equivalents of the mixed acids. In the following table results are given based on the melting-points only :

III.

Stearic acid.	Palmitic acid.	Barium acetate solution added. cc.	Melting-point. °C.	Approximate percentage of stearic acid in precipitate.
0.5	0.5	(1) 2.5	60.8	60–70
		(2) 2.5	54.6	about 30
1	1	(1) 2.5	59.4	60
		(2) 2.5	59.0	nearly 60
		(3) 2.5	58.6	50–60
		(4) 2.5	54.2	30
0.5	1	(1) 2.5	57.0	about 55
		(2) 2.5	55.8	" 50
		(3) 2.5	54.2	30
2.1	0.9	(1) 2.5	64.0	nearly 80
		(2) 2.5	65.0	80–90
		(3) 2.5	65.8	80–90
		(4) 2.5	60.5	60–70
		(5) 2.5	54.6	30–40

[1] *Ann. Chem. Pharm.*, 92, 295.

It is obvious from these results, that by means of an aqueous solution of barium acetate, used in the proportions stated, but a very moderate concentration of the higher fatty acid can be accomplished in one precipitation. Curiously enough, it not infrequently happens, that the second fraction contains a larger percentage of the higher fatty acid, than the first portion. Quantitative results cannot possibly be obtained.

Precipitation with Lead Acetate.—As it might be thought, that owing to the employment of an aqueous solution and the consequent somewhat sudden separation of the precipitate a less perfect fractionation took place than if the precipitate were allowed to form very slowly, we repeated the fractionation with the employment of an alcoholic solution of lead acetate. A solution, containing 6.67 grams of the salt in 100 cc. of alcohol, of which ten cc. were capable of completely precipitating one gram of stearic acid, was made, and the required amount of this solution was added slowly to the hot alcoholic solution of the mixed fatty acids. The fraction crystallizing out on cooling was treated as described in reference to the preceding table.

IV.

Stearic acid. Grams.	Palmitic acid. Grams.	Lead acetate solution added. cc.	Melting-point of liberated acids.	Approximate percentage of stearic acid. Per cent.
0.5	1	(1) 5	60.2	60–70
		(2) 5	55.0	30–40
		(3) 5	55.4	30–40

Here again the separation was no more complete than in Tables I and III.

Precipitation with Magnesium Acetate.—A solution containing 18.835 grams of magnesium acetate in 500 cc. of which ten cc. were required to precipitate one gram of stearic acid was made and used in the following experiment:

V.

Stearic acid. Grams.	Palmitic acid. Grams.	Magnesium acetate solution added. cc.	Melting-point.	Approximate percentage of stearic acid.
0.5	0.5	5	62	About 70

By these results we were confirmed in our opinion, that while by oft repeated fractionation a mixture of fatty acids may be

made to yield the highest fatty acid in a comparatively pure condition, by a single precipitation no sharp separation can even approximately be obtained however slowly the separation be allowed to take place. When more than two fatty acids are present in a mixture, the results must be still more doubtful. For quantitative analytical work, for which, of course, the method was never intended, it is not applicable.

After numerous attempts to separate the liquid and the solid fatty acid from each other by means of glacial acetic acid, which readily dissolves oleic, but at the same time not inconsiderable amounts of palmitic and of stearic acids, and by mixtures of acetic acid, alcohol and water (after the method of David[1]), we came to the conclusion that nothing like a sharp separation could thus be effected. Somewhat better were the results obtained by the use of dilute alcohol alone. On grinding up fatty acid, as obtained by the saponification of a solid fat and decomposition of the soap, with dilute alcohol (sp. gr. 0.911) in a mortar, we found that the unsaturated fatty acids were completely dissolved, the palmitic acid partially so, while the stearic acid remained almost completely undissolved. From ten to twenty grams of the various fatty acid mixtures were thus ground up with 100 cc. of dilute alcohol, the latter removed by a filter-pump and the residue was washed with 100 cc. of dilute alcohol of the same strength. After pressing the residue in a filter-cloth, placed between blotting paper, a pearly white mass was obtained, which after drying, showed an iodine absorption of from two to three per cent. From the molecular weight, ascertained by means of alcoholic alkali, the proportions of palmitic and stearic acids were calculated on the assumption that nothing but stearic and palmitic acids were present, an assumption which cannot be very incorrect, because the lower fatty acids are soluble to a considerable extent in alcohol of the strength mentioned.

[1] *Compt. rend.*, **86**, 1416.

VI.

	Fatty acids.	Washed residue.	Molecular weight.	Per cent. stearic acid in the washed acids.	Per cent. stearic acid in original acid.	Iodine number of original fatty acid.	Melting-point of original fatty acids.
	Grams.	Grams.					
Butter (Brittany)...	10	2.0	260.8	15.0	3.0	....	....
Same sample.....	..	..	259.3	....	....	....	....
	..	..	260.3	....	....	....	....
Butter (Danish)	20	2.5	263.6	29.0	3.6	....	....
	..	..	263.8	....	....	....	....
Butter (Danish)	10	1.85	258.0	7.0	1.29	....	....
Oleomargarine.....	10	4.0	267.3	428.	17.12	46.5	43.2
Margarine	10	3.7	266.2	40.0	14.8	43.23	38.0
Margarine	10	4.0	265.0	34.4	13.76	....	....
Mutton tallow	10	5.5	264.0	30.0	16.5	39.5	43.8
Mutton tallow	20	11.0	265.8	37.4	19.47	35.6	47.8
Lard.....	20	7.5	258.8	8.6	3.2	....	....
Lard.....	20	7.0	260.0	15.0	5.2	....	....

Although, when working under exactly the same conditions, fairly constant results could be obtained, the method effected at best only a concentration of the stearic acid and afforded no certainty that the final product consisted of only two fatty acids, from the equivalent of which the proportion might be calculated. Although we worked as nearly as possible at a uniform temperature, variations could not be avoided, leading us to abandon the search in this direction.

The following reasoning gave much greater hopes of success. Imagine a mixture of fatty acids to be treated with an amount of solvent sufficient to dissolve the whole of the various components of the mixture. If the solvent were already saturated with one of the constituents of the fatty acid mixture to be examined, it was to be expected that the totality of the corresponding fatty acid contained in the mixture would remain undissolved. Or, if a mixture were heated with a solvent saturated at a certain temperature with one of the constituents sought to be determined, then on cooling down to a corresponding temperature, the whole of the particular constituent might be expected quantitatively to crystallize out, provided that the other constituents of the fatty acid mixture exercised no restraining influence by adding to the solubility.

In principle this is the method of Casamajor for the quantitative separation of cane sugar from invert sugar. Casamajor washed the sugar to be examined with methyl alcohol saturated with cane sugar.

We chose the freezing-point of water as the most suitable constant temperature, it being easily maintained and the solubility of stearic and the other acids occurring in fats being suitable for accurate work.

After some preliminary experiments with ether and other solvents which we had to reject as taking up too much stearic acid, we finally fixed upon alcohol (methylated) of a specific gravity of 0.8183, containing 94.4 per cent. of alcohol by volume. It will be seen, in the following experiments, that the exact strength of alcohol is a matter of no consequence, but the solubility determinations here to be given apply only to alcohol of that strength.

For maintaining a constant temperature we employed an ice-chest, constructed of a metal box, to the interior side of which were soldered suitable sockets to receive the clamps necessary to hold the small flasks in which the determinations were carried out, submerged up to the neck in ice-water. The metal box was fitted in a wooden box and the space between metal and wood was packed with wool and saw-dust, while a cushion of wool and flannel was placed between the lids of the metal and wooden boxes.

For the preparation of the stearic solution about three grams of pure stearic acid were dissolved in about a liter of warm alcohol of 0.8183 sp. gr., and the stoppered bottle containing the solution was placed over night in the ice-water (in which were lumps of ice) in the chest, so that the bottle was submerged up to the neck. After twelve hours a considerable portion of the stearic acid had crystallized out. The saturated mother liquor was siphoned off without removing the bottle from the ice-water. The filtering siphon used consisted of a small thistle funnel twice bent at right angles, fitting with its smooth limb in a flask attached to a suction pump, while the bulb of the funnel, which was submerged in the ice-cold solution, was covered over with a piece of fine calico. On applying suction a perfectly clear stearic

solution was obtained, saturated at 0° C., or rather at 0.2° C., which was the temperature almost constantly shown by a standard thermometer.

A precisely similar mode of filtration was also adopted in the quantitative experiments on mixed fatty acids, the thistle funnel used being a miniature one, with a bulb not larger than about one-quarter of an inch in diameter. The accompanying drawing will sufficiently explain the apparatus.

VII.

SOLUBILITY OF STEARIC ACID IN ALCOHOL (SPECIFIC GRAVITY 0.8183), AT 0° C.

Stearic acid taken. Gram.	Alcohol. cc.	Time of cooling. Hours.	Residue obtained by evaporating ten cc. of the filtered solution. Gram.
0.2	100	12	0.0155
0.2	100	36	0.0153
0.2	100	84	0.0153
0.5	100	12	0.0158
0.5	100	36	0.0145
0.5	100	84	0.0140
0.3	100	48	0.0144
0.3	100	84	0.0142
0.3	100	12	0.0157
0.3	100	36	0.0149
0.4	100	12	0.0158
0.4	100	36	0.0148

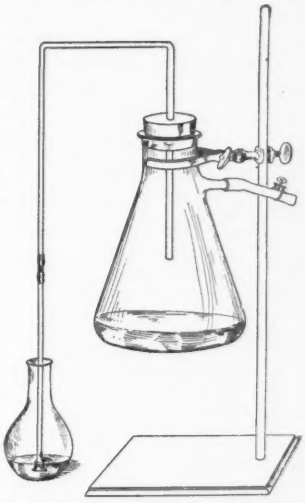
VIII.

SOLUBILITY OF PALMITIC ACID IN ALCOHOL (SPECIFIC GRAVITY 0.8183) AT 0° C.

Palmitic acid taken. Gram.	Alcohol. cc.	Time of cooling. Hours.	Residue obtained by evaporating ten cc. of filtered solution. Gram.
2	100	12	0.1298
2	100	36	0.1244
2	100	60	0.1211
2	100	84	0.1134
2	100	108	0.1086
2	100	132	0.1044
2	100	156	0.1028
2	100	12	0.1320

From the two preceding tables it appears that it is easy to obtain constant results with stearic acid, and that supersaturation does not readily occur. The solubility of the palmitic acid in alcohol of the same strength as that employed for stearic acid is about eight times greater than in the case of stearic acid, and constant results are far less easy to obtain.

Experiments with Known Amounts of Pure Stearic Acid.— Accurately weighed quantities of pure stearic acid were placed in weighed flasks capable of holding about 150 cc., provided with a rubber cork. From fifty to 100 cc. of the saturated stearic solution were added, the flask closed and the contents gently warmed on a water-bath till all stearic acid had dissolved. The flask was then clamped in the ice-chest and kept in ice-water over night. In the morning the contents of the flask were, as a rule, gently shaken, without being withdrawn from the ice-water, in order to promote crystallization and again left for at least half an hour. The alcohol was then filtered off by means of the arrangement described, care being taken to draw off the solution as completely as possible. The residue was washed three times successively with ten cc. of the saturated stearic solution, cooled down to 0° C. The small funnel was then detached from the suction arrangement and washed with hot pure alcohol, the washings falling into the flask containing the residue, the flask being previously taken out of the ice-chest. The alcohol was then evaporated, and the residue dried at 100° C. to constant weight.



Since the interior sides of the flask, as well as the residue of crystallized stearic acid, retained a small amount of the stearic alcohol, a small correction, experimentally found to amount to 0.005 gram had to be applied, this amount having to be deducted from the total weight found. In almost all cases the precipitated stearic acid formed a small, but compact mass after filtration, retaining a very minute amount only of the washing solution.

The following results were obtained.

IX.

Stearic acid taken. Gram.	Saturated alcohol. cc.	Total residue found.	Stearic acid after deducting 0.005 gram. Gram.
0.0188	100	0.021	0.016
0.0220	100	0.025	0.020
0.0320	100	0.0381	0.0331
0.0381	50	0.0445	0.0392
0.1072	50	0.113	0.108
0.1356	100	0.1414	0.1364
0.1414	100	0.1440	0.1390
0.2137	100	0.2206	0.2156
0.2282	100	0.2334	0.2281

As a check we also made a number of experiments by dissolving weighed quantities of the stearic acid in the saturated alcohol, leaving the flask over night in ice and, instead of weighing the crystallized deposit, evaporated measured quantities of the filtrate, thus determining the amount of stearic acid in solution. If this corresponded with the amount previously found to be soluble in ten cc. of alcohol, it followed that the whole of the added stearic acid had separated.

X.

Stearic acid. Gram.	Saturated alcohol. cc.	Residue in 10 cc. after twelve hours. Gram.
0.1955	100	0.0155
0.5090	100	0.0150
0.3130	100	0.0157
0.4010	100	0.0158

It will be seen that the amount left in solution perfectly corresponded with that contained in the stearic alcohol, and that therefore none of the added stearic acid could have remained in the solution.

Having thus satisfied ourselves, that pure stearic acid could be determined with a satisfactory degree of accuracy, it remained to be seen, whether in the presence of other fatty acids, equally satisfactory results could be obtained, or whether other fatty acids would themselves exercise a solvent action upon the stearic acid.

XI.

INFLUENCE OF LOWER SATURATED FATTY ACIDS.

Stearic acid taken. Gram.	Lower fatty acid employed. Gram.	Stearic acid found after deducting 0.005 gram. Gram.
0.0556	5 cc. butyric acid.	0.0582
0.0476	5 cc. acetic acid.	0 0468
0.0990	1.5 gram cocoanut fatty acids.	0.1070
0.1060	0.9079 cocoanut acids.	0.118
0.2020	0.5130 " "	0.220

XII.

INFLUENCE OF PALMITIC ACID.

Stearic acid taken. Gram.	Palmitic acid added. Gram.	Stearic acid found, after deducting 0.005 grams. Gram.
0.2026	0.5472	0.2032
0.1016	0.5354	0.1074
0.0520	0.600	0.055

Influence of Unsaturated Fatty Acids.—The oleic acid used for the following experiment was commercial oleic acid, and was not free from stearic acid. Three grams crystallized in the manner described from stearic alcohol, giving 0.025 gram of stearic acid. A corresponding deduction had therefore to be made in the following experiment:

XIII.

Stearic acid. Gram.	Crude oleic acid. Gram.	Stearic acid found. Gram.
0.2997	3.200	0.3355

Deducting from the latter figure 0.0278 gram, the amount of stearic acid obtainable from the three and two-tenths grams of oleic acid, and 0.005 gram for correction, there remain 0.3027 gram of stearic acid recovered from the 0.2997 taken, or one per cent. too much.

Influence of Saturated and Unsaturated Fatty Acids Together.—Fatty acids prepared from hog's lard were first crystallized by themselves and afterwards with different quantities of added stearic acid, with the following results:

XIV.

Lard acids taken. Gram.	Stearic acid added. Gram.	Stearic acid obtained. Gram.	Added stearic acid recovered. Gram.
0.5	none	0.0242	.....
0.5	0.050	0.0738	0.0496
0.5	0.080	0.1058	0.0816

It is thus shown, that stearic acid added to a mixture of fatty acids can be completely recovered in the manner described.

Experiments with Commercial Stearic Acid. — The sample employed had an iodine absorption of two and three-tenths per cent. and melted at 56.2° C.

XV.

Commercial acid taken. Gram.	Stearic alcohol added. cc.	Amount of deposit minus 0.005 gram. Gram.	Per cent. of stearic acid found.
0.1042	50	0.0490	47.02
0.1480	50	0.0702	48.7
0.2510	50	0.1223	48.7
0.2900	50	0.1468	50.6
0.3984	100	0.1932	48.5

XVI.

EXPERIMENTS WITH COMMERCIAL LARD.

Lard.		Iodine number.	Stearic acid minus 0.005 gram. Gram.	Stearic acid in fatty acids. Per cent.
1	0.9794	61.2	0.1338	13.06
2	0.5065	not taken	0.0635	12.53
2	0.8328		0.1090	13.08
2	1.0604		0.1359	12.90
3	0.4970	57.5	0.0801	16.11
3	1.0178		0.1634	16.05
4	1.0987	61.2	0.0669	6.09
4	0.9990		0.0764	7.6
4	1.2878		0.0782	6.07
5	0.5150	65.66	0.0548	10.64
5	1.0410		0.1030	9.89
6	0.5000	63.58	0.0372	7.4

Determination of Stearic Acid in Fat from Different Parts of the Same Pig.—It is well known that the proportion of liquid and solid fat varies very considerably in the fat taken from different parts of the same animal. We thought it would be of interest to ascertain whether in this case the alteration affected only the proportions of fluid (unsaturated) and solid fatty acids, or whether the latter themselves varied in composition. The animal from which the fat was taken was a Somersetshire pig six months old. The following table contains the results :

XVII.

Part of pig.	Fatty acids taken. Grams.	Melting-point.	Iodine absorption.	Stearic acid minus 0.005 gram. Gram.	Melting-point of deposit.	Stearic acid. Per cent.
Head	0.5212	34.8°	67.7	0.0452	67.8	8.67
"	1.0481			0.0993	66.2	9.47
Ham	0.5006	34.6	61.6	0.0438	67.5	8.74
"	1.0044			0.0906	67.3	9.02
Breast	0.5152	36.8	64.2	0.0610	67.2	11.84
"	1.0219			0.1114	66.8	10.90
Flare	0.4936	40.0	52.8	0.0774	66.5	15.70
"	1.0096			0.1450	67.2	14.40
Back	0.5002	35.6	67.9	0.0430	67.0	8.59
"	0.9998			0.0910	66.5	9.2
Flare from another pig:						
	1.5221			0.1940	67.2	12.70
	1.1320			0.1386	67.0	12.24

It will be observed that the melting-points of the deposits obtained were in all cases slightly lower than that of pure stearic acid, but a mere trace of liquid fatty acid would be fully sufficient to account for the depression.

Assuming that the iodine number measures only oleic acid, and that 100 parts of the latter absorb ninety parts of iodine, it is easy to calculate the percentage of stearic acid in the saturated fatty acids contained in the total fatty acids from the fat of the animal referred to. On making this calculation it is found that the following are the percentages of stearic acid in the saturated fatty acids: Head, 35.0 per cent.; ham, 28.1 per cent.; breast, 39.6 per cent.; flare, 36.4 per cent.; back, 36.1 per cent.

It follows that in the case of this particular animal, at least, the variation in the consistency of the fat from various parts was almost entirely due to fluctuations in the amount of oleic acid.

Stearic Acid in Fat from Different Parts of the Same Sheep.—The different specimens of fat were taken from a Scotch sheep eighteen months old:

XVIII.

Part of sheep.	Fatty acids taken. Grams.	Iodine No. of fat.	Melting point of fatty acids.	Stearic acid minus 0.005 gram. Gram.	Percentage of stearic acid.
Back	0.5280	61.3	41.4	0.1310	24.8
Neck	0.5324	48.6	42.2	0.0876	16.4
Breast	0.7146	58.2	33.8	Very slight.	About one.
Ham	0.5100	50.6	40.8	No deposit after 2 days.	
Kidney	0.5030	48.16	45.6	0.1318	26.2
"	1.0175			0.2820	27.7

Calculating, as before, the percentage of the stearic acid in the saturated fatty acids we find: Back, 78.0 per cent.; neck, 36.0 per cent.; breast, 3.0 per cent.; ham, none; kidney, 58.0 per cent. The ham fat was liquid at ordinary temperature and that from the breast almost liquid.

In connection with these numbers, the following experiments may here find a place.

The molecular equivalent of the fatty acids from the sheep-kidney fat was found by titration with potassium hydroxide to be 271.6. The iodine number was 48.16, corresponding to 56.0 per cent. of oleic acid, assuming the whole of the iodine absorption to be attributable to oleic acid. The amount of stearic acid found being 26.2 per cent., there remain 17.8 per cent. for other saturated fatty acids. Assuming these to be palmitic, the calculated equivalent of the fatty acids is as follows:

Oleic	acid,	0.56 × 282 =	157.92
Stearic	"	0.262 × 284 =	74.71
Palmitic	"	0.178 × 256 =	45.57
			277.90

A very fair approach to the 276.1 directly determined.

XIX.

DETERMINATION OF STEARIC ACID IN MISCELLANEOUS FATS.

	Taken.	Iodine No.	Stearic acid minus 0.005 gram. Gram.	Percentage in fatty acids.
Beef-stearine	0.3024	....	0.1516	50.19
"	0.4174	....	0.2131	51.05
Oleomargarine	1.0107	....	0.2295	22.00
"	0.5192	....	0.1104	21.26
"	1.1100	....	0.2630	23.6
Margarine 1	1.0035	....	0.2495	24.8
" 2	0.5000	....	0.0586	11.72
Horse kidney-fat	0.701	85.4	No deposit.	

	Taken.	Iodine No.	Stearic acid minus 0.005 gram. Gram.	Percentage in fatty acids.
Cotton 'stearine'	0.9945	....	0.0334	3.3
Stillingia tallow		22.87	No deposit.	
Cocoa-butter	1.0168	....	0.4064	39.9
"	0.9548	....	0.3878	40.6
Maize oil	5.4186	....	No deposit.	
Almond oil	5.0236	....	No deposit.	
Olive oil	5.5558	....	No deposit.	
Earthnut oil	1.0648	....	0.0751 (M. P. 67° C)	7.00

XX.

Examination of Lard Crystals Separated from Ether.—It is well known to those who are accustomed to test for beef stearine in lard, that the form of the crystals obtained from pure lard is subject to considerable variation. While from some lards (the softer kinds) nothing but broad plates with pronounced chisel-shaped ends are obtained, from the harder kinds (flare lard) bunches of more pointed, though still chisel-edged, broad needles, crystallize. When the crystals are repeatedly recrystallized from ether, they as a rule become more and more needle-like, until they are practically undistinguishable from beef stearine crystals. One of us illustrated this point some time ago, before the Society of Public Analysts, by the exhibition of a large number of photo-lantern slides. After finding the remarkable differences in the amounts of stearic acid contained in various parts of the fat of the same pig, stated above, we thought that determinations of stearic acid in lard crystals might throw light upon this subject. No one as yet has attempted to explain the cause of the difference between the shapes of lard crystals and of beef stearine crystals, and it is not known whether the phenomenon is due to different isomerides, or simply to the proportion of stearic to palmitic or other acids contained in the deposits.

140 grams of a sample of flare lard, with an iodine absorption of 57.5 and a stearic acid contents of 16.11 and 16.05 per cent. in the fatty acids, were dissolved in a liter of warm ether. This is nearly the proportion of ether to lard generally employed in Stock's mode of working the Belfield test. Next morning there was an abundant deposit of crystals, showing the characteristic chisel-shaped ends. The crystals were separated, a small por-

tion saponified and the free fatty acids obtained. They were found to contain 32.4 per cent. of stearic acid. The ethereal solution, poured off from the crop of crystals, was evaporated, and part of the resulting fatty residue was decomposed to obtain free fatty acids. These contained only fifteen per cent. of stearic acid.

The main crop of crystals was then recrystallized from ether. The crystals were now needle-shaped, but had still distinct chisel-shaped ends. The fatty acids obtained from these contained 47.6 per cent. of stearic acid, while the fatty acids obtained as before from the second solution contained 17.23 per cent. stearic acid.

For a third time the crystals were crystallized from ether. The percentage of stearic acid had now risen in the fatty acids from the crystals to fifty-nine per cent., while the fat in solution contained 33.2 per cent. This third crystallization was, in form, hardly distinguishable from beef stearine crystals.

It can hardly be doubted, from a consideration of these results, that the form of the beef crystals is solely due to a larger proportion of stearic acid, than can be obtained from a pure lard by a single crystallization. When it is considered that pure lard contains, as far as our results go, not more than about fifteen per cent. of stearic acid, while beef stearine contains fifty per cent., it is intelligible, that from a beef-stiffened lard a deposit with a larger percentage of stearine is likely to result than from lard alone. At the same time the subject is quite worthy of a much more extended investigation.

The results also show that very many crystallizations would be required to separate the glycerides of palmitic and stearic acids fairly completely, as has been pointed out by Heintz many years ago.

XXI.

Examination of Samples of Butter.—We have made considerably over one hundred determinations of stearic acid in butter fatty acids, utilizing for this purpose the fatty acids remaining behind in the Reichert method. In the large majority of cases no deposit at all, or only a very minute quantity separated from

the stearic alcohol. In some cases, however, phenomena apparently of supersaturation, occurred. Occasionally on examining the flasks after opening the ice-chest in the morning, the solution was perfectly clear, but after shaking the contents and leaving them for some time longer in the ice, a small, but increasing, crystallization formed. We have not quite concluded our investigation into the cause of this phenomenon, and as the question of the examination of butter, with a view to distinguish it from margarine mixtures, is of very great practical importance, we propose to deal with this part of the subject in a separate communication. Inasmuch as all constants which are now utilized for the discovery of admixtures with butter-fat, are occasionally breaking down, it would be a matter of obvious importance, if a constituent which is never absent from butter substitutes, *viz.*, stearic acid, could be shown to be absent from butter-fat, or to occur in it only in minute quantities. Analysts would then for the first time be in a position to distinguish absolutely between pure and adulterated butter. For the purpose of the investigation we would thank those of our colleagues who take an interest in the subject to kindly furnish us with small samples of undoubtedly genuine butters, normal and abnormal, together with their results of analysis, including any or all of the following: Reichert number, insoluble fatty acids, refractive index, together with any details that may be of interest or importance.

XXII.

On the Abnormal Behavior of Palmitic Acid Obtained from Japan Wax.—Japan wax, consisting or supposed to consist mainly of palmitine with free palmitic acid, is considered to be a ready source of palmitic acid. We prepared a quantity of the acid from Japan wax, possessing apparently all the properties of palmitic acid. On making mixtures of this acid with known amounts of stearic acid, we were surprised to find that only a part, or none at all, of the added stearic acid could be obtained by crystallization from stearic alcohol, as the following figures will show:

Stearic acid. Gram.	Japan-wax acid. Gram.	Time of standing.	Stearic acid found. Gram.
0.1440	0.5	8 days	0.0438
0.2500	0.5	12 hours.	0.1542
0.0200	0.5	12 hours, turbidity only.	
0.2000	0.5	60 hours.	0.1800
0.4000	0.5	12 hours.	0.3800
0.2370	0.5	4 days.	0.2217
0.1500	0.5	4 days.	Turbidity only.
0.1000	0.100	12 hours.	Very slight precipitate.
0.0500	0.1	3 days.	" " "
0.05	0.2	"	" " "
0.025	0.225	"	" " "
none.	0.5	2 days.	none.

Without extended investigation it is impossible even to guess at the reason of the abnormal behavior of Japan-wax acids. Whether they combine with the added stearic acid, or cause the latter to be etherified by the alcohol, we are unable to say. The whole subject of Japan wax is quite worthy of investigation, as the statements made concerning it are somewhat contradictory. In any case, the failure to apply our method to Japan-wax acids does not directly bear upon the question of determination of stearic acid in ordinary fats and oils, in which we are quite satisfied that acid can be determined with reasonable accuracy.

The principle underlying the method described may be applied also to the determination of other fatty acids, such as palmitic and arachidic. In the former case the results would of necessity be less exact on account of the far more considerable solubility of palmitic acid and the greater correction number to be applied. For arachidic acid, on the other hand, the method ought to do good service, as it may safely be assumed that its solubility is far less than that of stearic acid. We hope to recur to the subject at some future time.

To summarize in a few words the method which we recommend :

Prepare a supply of alcohol saturated with pure stearic acid, or with stearic acid containing not much palmitic acid, at 0°C. Dissolve from one-half to one gram of the fatty acid mixture to be examined, if these are solid, or about five grams if fluid, in about 100 cc. (exact measurement is not necessary) of stearic alcohol. Leave in an ice bath over night, agitate the mixture next morn-

ing and allow to stand in ice for a short time, filter off while the mixture remains in ice, wash with stearic alcohol at 0° C., dry and weigh. Determine the melting-point of the product, which should not be much less than 68.5° C.

11 BILLITER SQUARE, LONDON, Nov. 23, 1896.

THE DETERMINATION OF SOLID FATS IN COMPOUND LARDS.

BY GEORGE F. TENNILLE.

Received December 11, 1896.

IN March, 1896, there appeared in this Journal an article by J. H. Wainwright entitled, "The Determination of the Solid Fat in Artificial Mixtures of Vegetable and Animal Fats and Oils."

Samples of compound lards had been submitted to the United States laboratory for the determination of the relative proportion of their constituents in order that the claim of the exporters for "drawback" of duties paid on one of the constituents might be verified, and the paper consisted in a description of a mechanical process which had been adopted by the United States laboratory for use in such determinations.

Though no great claim for accuracy in results or of scientific principles involved was made yet the conclusion arrived at was that the process would give correct results to within about one and one-half per cent.

Having been connected with one of the companies interested in the collection of this "drawback" of duties paid on the oleostearine used in compound lard, and having personally supervised the making of the lard which was sent to the United States laboratory for analysis, and hearing that the result obtained by the chemist often fell short of the actual amount of oleostearine which I knew to be contained in the samples, I made a great many trials of the process and came to the conclusion that, though under certain conditions it might give concordant and fairly accurate results, it could not be relied upon at all under certain other conditions.

I have selected a series of ten from the many analyes which were made with a view of showing in a rather exaggerated manner perhaps the possible results when the test is carried out under those conditions which prohibit accuracy.

The process was carried out by me essentially as described in this Journal, **18,** 259, except in two particulars.

Firstly, the sample after the preliminary melting and slow cooling to 75° F. was allowed to stand at exactly that temperature for twenty-four hours before subjecting to pressure, instead of "standing over night at ordinary temperature," as described by the author of the process, and secondly, twenty-five grams of the sample instead of fifty were used in the screw press.

These ten samples each contained twenty per cent. oleostearine and eighty per cent oil.

		Grams.
	No. 1.	
Oleostearine.	Titre 50.6° C	20
Cotton-seed oil.	A very heavy bodied oil	80
	No. 2.	
Oleostearine.	Titre 50.6° C	20
Cotton-seed oil.	A moderately heavy bodied oil	80
	No. 3.	
Oleostearine.	Titre 50.6° C	20
Cotton-seed oil.	An ordinary oil	80
	No. 4.	
Oleostearine.	Titre 50.6° C	20
Cotton-seed oil.	An ordinary oil	80
	No. 5.	
Oleostearine.	Titre 50.6° C	20
Cotton-seed oil.	A very light bodied oil	80
	No. 6.	
Oleostearine.	Titre 46.2° C	20
Cotton-seed oil.	The same oil as in No. 1	80
	No. 7.	
Oleostearine.	Titre 46.2° C	20
Cotton-seed oil.	The same oil as in No. 2	80
	No. 8.	
Oleostearine.	Titre 46.2° C	20
Cotton-seed oil.	An ordinary oil	80
	No. 9.	
Oleostearine.	Titre 46.2° C	20
Cotton-seed oil.	An ordinary oil	80
	No. 10.	
Oleostearine.	Titre 46.2° C	20
Cotton-seed oil.	The same oil as in No. 5	80

The following are the percentages of solid fat which were obtained by Wainwright's method on these samples:

Samples.	Per cent.
No. 1	28.14
" 2	26.83
" 3	21.07
" 4	23.77
" 5	18.10
" 6	21.71
" 7	19.43
" 8	16.77
" 9	16.10
" 10	13.13

Cotton-seed oil, as every one is aware who has ever handled it to any great extent, varies in the relative amounts of its chief constituents.

For instance, a natural sample of cotton-seed oil may be of such character that it will remain a limpid liquid for any length of time at a temperature of 32° F.; another oil may deposit stearine at as high a temperature as 80° F., may be a viscous liquid at 65°, and a hard brittle fat at 32° F. Such oils, of course, are unusual and are extremes not often met, but they do occur and may come to the refiner and be used in the manufacture of his compound lard.

Again, oleostearine differs in its constitution, but here the differences are due to the process of its manufacture and not to the processes of nature as in the cotton-seed oil.

The temperature at which the oleo stock is pressed and the amount of pressure applied, which variations may be due to the state of the markets for oleo oil and oleostearine, or due to the carelessness of the workman, effect the composition, and therefore the hardness of oleostearine.

In the examples given above I have chosen purposely an unusually hard stearine and one of unusual softness; an extremely heavy bodied cotton-seed oil, a moderately heavy bodied cotton-seed oil, four ordinary cotton-seed oils, and one of unusual light body.

On running titre tests on the cakes obtained in the screw press it was found that they were within a fraction of a degree in each case of the titre of the oleo which had been used in the samples, thus showing that the pressure in the screw press had been sufficient to insure accurate results if the suppositions upon which the process was based were correct; namely, that from a

mixture of oleostearine and cotton-seed oil, which had been melted and cooled and allowed to stand at a moderate temperature for some hours, all of the oleostearine would crystallize out, and all of the oil remain a liquid.

The cakes were also tested qualitatively for cotton-seed oil and were found to contain it. The oil drained off from the pressing was also tested for beef fat and found to contain it.

It would seem from an examination of the above results that a cotton-seed oil which had a very heavy body, that is, which would easily deposit stearine at ordinary temperatures, when subjected to this process will add some of its stearine to the oleostearine crystallizing from the mixture and render the results too high; that an ordinary cotton-seed oil gives up very little stearine to the cake but has a tendency to dissolve or keep in solution a portion of the beef fat, a greater portion the softer the beef fat; that a light bodied cotton-seed oil, having comparatively very little stearine in its composition and being capable of dissolving a greater amount than an ordinary oil, has a tendency to do so, and keeps more of the beef fat in solution and the more the softer the beef fat.

A very hard oleostearine has a tendency to make the cakes heavier, owing to the difficulty in pressing out the last portions of the oil.

A very soft oleostearine has a tendency to make the cakes lighter, for a portion of the liquid glycerides contained in it may be pressed out with the oil.

It is evident then, that this process of determining the relative amounts of the constituents of compound lard cannot be relied upon. It may, indeed, under ordinary conditions, give results which may very easily be within one and one-half units of the true percentage, but if the conditions be at all varied, and they are very likely to be varied, the results may be at least seven or eight per cent. too high or low.

ESTIMATION OF BORIC ACID IN FOODS.

By L. de Koningh.

Received November 13, 1896.

THE estimation of boric acid, at one time very troublesome, has become quite an easy matter since the discovery that it may be accurately titrated in presence of glycerol with phenolphthalein as indicator. To apply the process to articles of food, (and I will confine myself for the present to milk and uncooked eggs,) some few precautions must, however, be taken.

Boric acid is seldom used alone, but mostly in admixture with borax, a mixture of three parts of the acid with one part of ground borax, constituting the article known as *glacialine*. In practice it is, however, in my opinion, not necessary to make a distinction between the acid and its sodium salt, as both are no doubt equally harmless in small quantities; but if the amount of either reaches one per cent. or more the time has come for a protest.

When testing uncooked eggs (the entire contents beaten up) for boric acid, I take five grams of the sample, add one drop of sodium hydroxide (1 : 1), dry, and finally incinerate. The char is then powdered, boiled with water, and the residual black mass again burnt. The ash is also boiled with water and the two solutions are united. The liquid is now faintly colored by methyl orange and tenth-normal sulphuric acid is added until a faint pink is obtained. The solution is now boiled for a minute to expel carbon dioxide, cooled, mixed with one-half of its bulk of glycerol, and titrated with tenth-normal sodium hydroxide, with phenolphthalein as indicator. Although it is now admitted that in presence of glycerol the amount of acid may be calculated from the number of cubic centimeters of sodium hydroxide used, I prefer to check my sodium hydroxide with pure crystallized boric acid, using about the same quantity as present in the sample, and mixing this up with exactly the same amount of glycerol and water. Working in this manner the estimation of boric acid is, as regards accuracy, second to none.

It must, however, be remembered that eggs contain a small quantity of alkaline phosphates, and that phosphoric acid behaves somewhat like the boric acid. A method of removing this acid has already been proposed and is based on the insolu-

bility of calcium phosphate and the *comparatively* large solubility of the borate. I find, however, that in uncooked eggs there is just enough phosphoric acid to account for three cc. tenth-normal sodium hydroxide, when working on five grams of sample, so I now propose to deduct three cc. of sodium hydroxide from the number of cubic centimeters taken by the sample. I scarcely need point out the necessity of proving the acid by the alcohol test. As a rule the presence may be ascertained by simply stirring some of the sample with a drop of sulphuric acid and a little spirits of wine and then setting fire to it.

When dealing with milk I allow one cc. of sodium hydroxide for every ten grams of the sample. If the amount of acid is, as usual, very small, no particular accuracy can be claimed for the process; but if present in larger and, consequently harmful quantity, the results are all that may be desired.

LONDON, ENG., JUNE, 1896.

A STUDY OF THE CLARIFICATION OF SUGAR CANE JUICE.[1]

BY J. L. BEESON.

Received December 3, 1896.

THE clarification of the cane juice, so important a factor in the manufacture of sugar, is practically the same in method as that in use by the planters of Louisiana one hundred years ago. The method consists in the addition of slaked lime or milk of lime to the cold juice until neutrality or slight alkalinity is reached; then the temperature of the mass is raised nearly to boiling, when a coagulum forms and is carried to the surface by the upward motion of the liquid, and there forms a thick dark green scum called "the blanket." This is removed by skimming, and calcium superphosphate solution (called clariphos), is added until the juice begins to brighten in color. The method is, in the main, an empirical one, the nature of the bodies removed and the chemical changes involved therein not being understood. The practical sugar boiler has virtually no facts to guide him in this important branch of his work. It was therefore the object of this investigation to compare the juice expressed by the mill with that obtained from the same large sample of cane obtained by

[1] This work was done in the laboratory of the Audubon Sugar School, New Orleans, which institution was discontinued last July.

the process of diffusion with hot water. Also to compare these juices before and after clarification, and to study the products so removed. The methods of analyses used were those adopted by the Association of Official Chemists. The total proteids and albuminoids were obtained by multiplying the total and albuminous nitrogen by the factor 6.25, the difference being termed amids. The "gums" or non-nitrogenous solids not sugars, were obtained by subtracting the total proteids and ash from the "solids not sugars." Since the diffusion juice is more dilute than the mill juice, the results of the former were calculated to the same total solids of the mill juice for the sake of easy comparison. These analyses were made in duplicate throughout. Below is given the results of these analyses:

ANALYSIS I.

	Total solids.	Sucrose.	Glucose.	Solids not sugars.	Purity co-efficient.	Ash.	Gums.	Total proteids.	Albuminoids.	Amids.
Mill juice.....	14.9	10.8	2.03	2.07	72.5	0.413	1.385	0.292	0.099	0.193
Diffusion juice	14.9	11.4	1.87	1.63	76.5	0.448	0.93	0.224	0.065	0.179
Clar'fi'd diffu'n juice	14.9	11.3	1.97	1.63	75.9	0.456	0.97	0.204	0.056	0.148

By comparing the juice from the mill with that obtained by diffusion with hot water, it will be seen the latter contains less solids not sugars, less total proteids, less albuminoids and amids than the mill juice. This would indicate that the hot water had, during the process of diffusion, coagulated and left behind in the begasse about one-third of both the albuminoids and gums, in which case analyses of the begasse from these two sources should show more albuminoids and gums in the diffusion sugars. Estimation of the gums was not attempted, but estimation of the total proteids in the two bagasses showed an excess in that from the diffusion, as will be seen below:

ANALYSIS II.

	Per cent.
Bagasse from mill, proteids	1.146
Bagasse from diffusion process, proteids.....	1.731

This analysis was repeated with mill and diffusion bagasse of another variety of cane, showing as before a larger percentage of proteids in the latter.

By comparing the clarified with the unclarified diffusion juice it will be seen that there was a further, but much smaller, removal of the albuminous bodies by the action of lime and heat in the process of clarification. But there was a slight increase in ash and what is estimated as gums, attended by a lowering of the coefficient of purity of the juice. The increase in ash doubtless accounts for the increase in what is termed gums, for the lime had combined with the free acids in the juice, most of which acids identified in the juice form soluble compounds with lime. Then it is a well known chemical fact that hot alkaline solutions will decompose amids with the liberation of ammonia, forming the alkaline salts of the acid of the amid. This would further augment the lime salts in the juice. The decrease in amids in the clarified juice in this case would indicate that this decomposition of the amids had taken place during the heating and skimming. If the juice were sufficiently alkaline and the heating prolonged, we should expect the albuminoids to be broken down into their constituent compounds, reducing sugars, amids, etc., and the latter broken up into ammonia and lime salts of the acid of the amid. This would decrease the albuminoids, as is true in the above case, as well as increase the lime salts in solution. It is clear that excessive use of lime and heat would decrease the purity of the juice, as is noticed in this case. These analyses were repeated with five different kinds of cane, each time showing results similar to the above. This lowering of the purity of the juice by clarification was doubtless due to the presence of an excess of lime due to the solution of the larger particles of lime during the heatings and skimmings, for an analysis of the settlings in the bottom of the clarifying tanks showed about fifty per cent. of lime. This trouble, of course, could be remedied by using lime which had been ground to an impalpable milk with water in a mill. This would approximate a true solution. Lime-water cannot be used on account of the dilution it effects. The amount of ash in the clarified juice depends upon the original acidity of the juice and the amount of calcium superphosphate added after skimming. If more be added than is required to remove the free lime, there might be a lessening of the ash, but this would again set free the acids in the juice,

which might cause considerable inversion during the subsequent heatings and evaporations.

Below is given the analysis of the products removed by the clarification:

ANALYSIS III. OF SKIMMINGS.

	Per cent.
Ash	26.84
Proteids	15.52
Gums and acids	57.52

The relatively small quantities of albuminoids in this coagulum would indicate that some of these bodies had been broken down by the clarification, as was previously suggested, and the presence of so large quantities of ash and non-nitrogenous bodies would indicate the formation of lime compounds. Upon comparing the three juices in Analysis I it is clear that the greatest purging of the juice was effected by heat alone during the process of diffusion, removing a third of the albuminoids and gums in the juice, the lime or heat in the clarification removing a further portion of the albuminoids, but increasing the non-nitrogenous bodies of the juice. What would be the relative effect if lime were added first and then heat applied? Which is the clarifying agent, lime, or heat, or both? In order to throw light upon these questions the following experiment was performed: To one liter of cold mill juice, clear lime-water was slowly added. After the acidity of the juice had disappeared (about ten cc. were required), a dark greenish precipitate appeared and continued to form as the lime-water was added until a faint alkalinity was reached, requiring 190 cc. more of the lime-water. This precipitate was carefully collected, dried at 100° C., weighed and analyzed. Then a few drops of calcium superphosphate solution were added until the juice began to brighten, in order to remove the small quantity of free lime. The juice was then heated for twenty minutes to 90°–95° C., when a small coagulum was formed. This was collected, dried, weighed and subjected to analysis. Many sugar houses pass sulphur dioxide into their juices before clarifying with lime and heat. In order to see if sulphur dioxide removed any bodies which lime and heat would not, a portion of the above juice was saturated with sulphur dioxide gas and heated. The juice was bleached, but no further

precipitate was formed. But this does not show that sulphur dioxide will not reduce certain organic bodies to compounds removable by lime and heat which would not otherwise have been removed by these agents. No experiments could for lack of time be made to settle this important point. Below is given the analysis of the juice before and after the lime-heat clarification:

ANALYSIS IV.

Mill juice.	Total solids.	Sucrose.	Glucose.	Solids not sugars.	Purity coefficient.	Ash.	Gums.	Total proteids.	Albuminoids.	Amids.
Unclarified	14.9	11.32	2.54	1.04	75.9	0.309	0.602	0.131	0.109	0.0224
Clarified	14.9	11.91	2.37	0.72	79.4	0.301	0.365	0.062	0.041	0.021

ANALYSIS V. OF THE PRODUCTS REMOVED BY CLARIFICATION.

	Ash.	Albuminoids.	Gums.
Precipitate with lime, weight in 100 grams juice, 0.266 gram	20.6	18.06	61.54
Coagulum from heating afterwards, in 100 grams juice, 0.025 gram ..	11.5	37.28	51.25

The clarified juice was much clearer and lighter in color than the unclarified. By comparing the constituents of the two juices one by one it will be seen that there is a marked improvement, due to clarification when the process is carefully carried out. The lime-heat clarification has removed over half of the albuminoids, and nearly half of the gums, resulting in a loss of about one-third of the solids not sugars, and an increase in the coefficient of purity of about four per cent. of the juice. By applying the results in Analysis V to those in Analysis IV, it will be seen that the lime alone, when added first, has removed about forty-eight per cent. of the entire albuminoids, and about thirty-six per cent. of the entire gums in the juice, whereas heat alone applied first (Analysis I) removed about thirty-five per cent. of the albuminoids and forty per cent. of the gums. From this it would appear that lime is in general the more effective purging agent, removing decidedly more of the albuminoids, but less of the gums than heat. From Analysis V it will be seen that of the total organic matter removed, nearly ten-elevenths were removed by the lime. Of the albuminoids removed, four-fifths were removed by the lime, and of the gums nine-tenths, the remaining portions of both the albuminoids and gums being removed

by the heat. It is quite clear that the lime has formed insoluble compounds with both the gummy bodies and the albuminoids, the latter forming calcium albuminates, probably similar to the better known copper albuminates. But the lime does not combine with all of these bodies in the juice, or if it does the compounds are soluble. The lower percentage of ash in the coagulum would indicate that if such soluble but coagulable compounds were formed, they were of a different nature, containing less lime. The albuminoids and gummy bodies in cane juice may then be divided into three classes: (*a*) Those which form insoluble compounds with lime, (*b*) those which are precipitated by heat, and (*c*) those which are not rendered insoluble by both lime and heat, the gummy bodies of class *c* being precipitable by nitrate of mercury and the albuminoids by copper hydroxide. Class *c* constitutes nearly one-half of these bodies in the cane juice. It is the further work of the sugar chemist to discover some cheap non-poisonous agent which will remove this class of bodies from the cane juice.

A NEW FORM OF PYKNOMETER.[1]

By J. C. Boot.[2]

Received November 9, 1896.

OF all the different forms of pyknometers, Fig. 1 represents the one that is probably most generally used.

Working with this form in a room where the temperature is much higher than the normal, there is one difficulty to contend with, which is, that in the time it takes to dry and weigh the pyknometer the liquid is continuously running out of the capillary tube in the stopper.

Fig. 1.

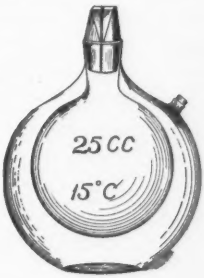


Fig. 2.

For the purpose of making accurate specific gravity determi-

[1] *Chem. Ztg.*, 1896, 20, 63.

[2] Read before the New York Section of the American Chemical Society, Nov. 6, 1896.

nations under such conditions, that is to say, when the temperature of the balance room is high, I have constructed a pyknometer with double walls, as shown in Fig. 2, in which the space between the two walls is carefully exhausted.

The apparatus is used in the following way:

Take for example a pyknometer of twenty-five cc. capacity and a normal temperature of 15° C.

Of the liquid, whose specific gravity is to be determined, we take about fifty cc. in a small flask and cool down to about 12° to 13° C.; a thermometer divided into $\frac{1}{10}$° or $\frac{1}{5}$° is used for noting the temperature.

After shaking the contents of the flask, wash out the pyknometer with about five cc. of the liquid, throw away these five cc. and then run in about twenty cc. The temperature of the liquid in the pyknometer will probably be about 14° C.

This twenty cc. are poured back into the flask and again about twenty cc. of the liquid are poured into the pyknometer. The temperature will now be about 14°.2 C.

This pouring of the twenty cc. into the pyknometer and then back into the flask is continued until the temperature of the liquid is 15° C.

We then fill up the pyknometer until it overflows and put in the stopper.

The apparatus can now be carefully dried and weighed without danger of any of the liquid running out of the capillary tube.

In this pyknometer, as shown in Fig. 1, it often happens that when drying, the simple pressure against the glass sides causes the liquid to run out through the capillary tube. Naturally this is impossible with my pyknometer.

The apparatus has proved very satisfactory. It weighs about thirty grams, and is made by Eimer & Amend, New York, and by Christ Kob & Co., Stützerbach, Germany.

THE CAFFEIN COMPOUND IN KOLA.[1]

By James W. T. Knox and Albert B. Prescott.

Received December 19, 1896.

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HISTORICAL.

Although the literature of kola extends back more than three hundred years, its chemical history is comparatively recent and may be briefly summarized as follows:

To Attfield[2] belongs the credit of proving that kola contains caffein; his work was done at the instance of Dr. Daniell,[3] who had made quite a study of the uses of kola among the natives of Western Africa, and who suspected from its physiological effects

[1] From the Proceedings of the American Pharmaceutical Association, 1896. Communicated by the authors.

[2] *Pharm. J. Trans.*, 1865, (2) **6**, 457.

[3] *Pharm. J. Trans.*, 1865, (2) **6**, 450.

that it contained a stimulating principle similar to that of coffee and tea. Their supply of material was limited and they seem to have carried their investigation into its chemistry no further.

In 1882 Heckel and Schlagdenhauffen[1] reported a more complete analysis of kola differing especially from that of the earlier workers in that it showed, in addition, the presence of theobromin and tannin. Heckel also noticed that a body was present which seemed to him to present considerable analogy to cinchona red, and he applied the name "kola red" (rouge de kola) to it. This, he afterwards found, gave a sublimate of caffein upon heating sufficiently, and he supposed the alkaloid to be retained mechanically, although he was unable to remove it by prolonged treatment with chloroform.

Knebel,[2] working in the Pharmaceutical Institute at Erlangen under the direction of Prof. Hilger (now at Munich), took up the investigation at this point in 1892, and isolated a tannin-like body to which he ascribed the formula $C_{14}H_{13}(OH)_6$ and which he named "kola red." This is not to be confounded with the kola red of Heckel, for Knebel considered Heckel's product an indefinite mixture, or rather an impure form of a glucoside which he (Knebel) believed to be present in kola, and which he believed to be composed of equal molecular proportions of caffein, glucose, and "kola red." This glucoside he called "kolanin," and, although he had only the dry seeds of kola to work upon, he inferred, from the proportions of caffein and glucose found therein, that in the fresh seeds no caffein was free. He inferred that the whole was combined in the glucoside, which under the influence of a diastatic ferment (which he isolated), with air and moisture, was partially decomposed, during the process of drying, into its component parts.

This hypothesis also seemed to explain why different workers, using different samples of the drug, had failed to get uniform results in the yield of caffein, for only the free alkaloids are removed by the immiscible solvents usually employed in assaying, combined alkaloids remaining behind. Different conditions in drying would give a variable extent of decomposition of this

[1] Heckel and Schlagdenhauffen, 1882 : *Repert. de Pharm.*, p. 163.
[2] E. Knebel, 1892 : *Apoth. Ztg.*, 7, 112.

(hypothetical) glucoside, and consequently afford discordant results in assaying.

Prof. Dr. Hilger[1] had noticed the apparent untrustworthiness of the usual assay methods in the examinations of cacao as well as of kola and was led by Knebel's results to investigate the chemistry of cacao, working at Erlangen. He succeeded in separating a glucoside from cacao analogous to the one Knebel supposed to be present in kola, and which yielded on hydrolysis with dilute mineral acids, theobromin, dextrose, and cacao red, $C_{17}H_{12}(OH)_{10}$, similar to kola red. The dextrose formed with phenylhydrazin a glucosazone of melting-point 204° C. Later,[2] at Munich, he applied the same and similar methods to kola, using the fresh seeds, and obtained a body, the "kolanin" of Knebel, yielding caffein, dextrose, and kola red on decomposition with dilute mineral acids, or diastatic ferments. He also describes in his paper his method for separating the ferment of kola, these details having been omitted from Knebel's original article.

Prof. Dr. Hilger has also kindly sent us the Inaugural-Dissertation[3] of Schweitzer for which we here make grateful acknowledgment. Schweitzer continued the work on kola and cacao, begun by Knebel and Hilger, verifying their results. His work on the (supposed) glucoside of kola indicates the combination of one molecule each of caffein and kola red, and three of dextrose, instead of one of each as claimed by Knebel. He proposes the formula $C_{40}H_{66}N_4O_{21}$ for "kolanin."

Another feature of his work on kola is, that while in the free alkaloids the proportion of caffein is to theobromin as 98.8 to 1.2, in the glucoside, he found it to be 80.3 of caffein to 19.7 of theobromin.

Of American workers, Schlotterbeck[4] and Topping[5] have done good service; Dohme and Engelhardt[6] have published reports of comparative assays of African and West Indian kolas. They found the African superior.

[1] A. Hilger, 1892: *Apoth. Ztg.*, 7, 469.

[2] A. Hilger, 1893: D'tsch. Vierteljahresschrift f. öffentl. Gesundheitspflege, 25, 559. Drittes heft.

[3] Carl Schweitzer, 1895: Inaugural-Dissertation zur Erlangung der Doktorwuerde, Munich.

[4] Kola: Monograph by J. O. Schlotterbeck, Detroit, 1894.

[5] C. O. Topping, 1894: *Proc. Am. Pharm. Ass.*, p. 178.

[6] Dohme and Engelhardt, 1896: *Am. Drugg.*, p. 12.

Other recent contributors are Kilmer,[1] whose paper is principally a compilation and Jean,[2] who examined a number of commercial preparations of kola, *i. e.*, its fluid extracts, tinctures, and wines.

A partial plant analysis of kola was made last year by one of us, with Prof. Schlotterbeck.[3]

THE SAMPLE.

Through the liberality of Messrs. Frederick Stearns & Co., Manufacturing Pharmacists of Detroit, Michigan, we were supplied with a large original package of kola nuts, just as imported by them from West Africa. The basket had not been opened, and the seeds were perfectly fresh, and were fine specimens. The best of these were selected, and as a means of preservation they were sealed up air-tight in clean and dry glass-stoppered jars. In about one-half the number of jars the air was displaced by dry carbon dioxide, and in a few others the red and white seeds were put up separately. That the carbon dioxide did not inhibit fungus growth, was shown by the appearance after five month's duration of a slight moldiness on some of the seeds put up in this atmosphere as well as on those preserved in air. This was not universally the case. At this time, after the expiration of nine months, we have several jars of the drug put up in exactly the same way, and at the same time in which the seeds are fresh and sound. Those preserved in carbon dioxide are somewhat paler, but internally are apparently unchanged, and a greater proportion of the seeds in this atmosphere, remained in prime condition, so that there would seem to be a slight advantage in its use. It is a rather remarkable fact that in those jars containing only red or only white seeds, there was no perceptible decomposition or fungus growth, and this regardless of the atmosphere used.

Action of Solvents.—When fresh kola seed is cut or bruised a chemical change immediately takes place, as shown by the rapid change of color of the cut surface from pink or cream-color to red-brown.

Desiring to avoid any decomposition of the drug in handling, a solvent was sought which would remove the active constituents

[1] F. B. Kilmer, 1896: *Am. J. Pharm.*, **68**, 96.

[2] J. Jean, 1896: *Repert. de Pharm.*, (3), **7**, 49.

[3] Knox and Schlotterbeck, 1895: Analysis of Kola, *Proc. Am. Pharm. Ass.*, p. 334.

without change. Water, absolute alcohol, ninety per cent. alcohol, fifty per cent. alcohol, ether, chloroform, benzene, acetone, ethyl acetate, dilute ammonia water, dilute potassium hydroxide solution, one per cent. hydrochloric acid, alcohol containing one per cent. of acetic acid, and glycerin, were the principal solvents tried. All were objectionable because the red coloration appeared almost immediately on contact of the cut surface of the drug with the liquid, coloring the solvent, if the coloring matter were soluble therein. Slicing the seeds under the surface of any of these liquids apparently neither retarded nor modified the formation of color.

Water was at first colored red, but gradually became turbid from precipitation of a portion of the matter at first dissolved; the alcohol of either strength gave a rich wine-red solution, which was permanent. The immiscible solvents removed only alkaloids and fat; both fixed and volatile alkalies developed an intense dark crimson color, changing to light scarlet on addition of excess of mineral acids, which change was accompanied by precipitation of a reddish flocculent substance; dilute acids heightened the color somewhat; glycerin seemed only to dehydrate the tissues without exerting solvent power.

Action of Heat.—This coloration has usually been ascribed to the activity of a diastatic ferment, and, therefore, recalling the action of heat on such bodies, it was decided to try the effect of sterilization on this drug. Accordingly a seed was sliced, the slices being received in boiling water. No coloration took place then or afterwards, a few seconds contact with the boiling water being sufficient to prevent its appearance. Further experimentation showed that up to 60° C. the heat augmented the production of color; from 60° to 65° it was somewhat retarded, and above 65° the slices retained their natural color.

On account of the starch present in kola, and for other reasons, the use of water was objectionable, so boiling alcohol was substituted successfully, and has been used exclusively by us for this purpose ever since. A temperature of 45° C. is sufficient when alcohol is employed to "coagulate the ferment," at least to prevent the coloration afterwards. Boiling chloroform and boiling acetone were each tried, but without successful results. Without

further discussion of the action of solvents, it may be remarked that, for pharmaceutical purposes and any others, when it is desirable to extract all the active constituents from kola with a single menstruum, our experience has shown that alcohol of not less strength than U. S. P. dilute alcohol is the most satisfactory agent.

Action of Cold.—It has been stated[1] that extreme cold seems to destroy the power of this ferment. An experiment, next described, seems to show that cold does not impair the potency of the ferment, but rather seems to preserve it. Two white kola seeds were sealed up in a dry bottle and immersed in a freezing mixture for three hours. On thawing, the production of the red-brown color was very rapid both upon cut and whole surfaces.

ASSAY OF KOLA.

Common Causes of Error.—Of the numerous methods proposed at various times by different workers for the assay of this drug, none has proven satisfactory and reliable. Many of these do not account completely for the free alkaloids of kola, and not at all for the combined alkaloids; others perhaps indicate pretty well the proportions of free alkaloids. Still, concordant results are not obtained, and the published assays of kola have a wide range of variation. Two reasons for these discrepancies have suggested themselves to us. First, insufficient knowledge of the properties of the combination bearing caffein has prevented the use of proper methods to secure complete liberation of the alkaloids from it; second, the caffein obtained is *weighed*, in a state of greater or less purity, varying with the method used and the care and judgment of the worker. It is not difficult to perceive how errors might thus be introduced.

We have worked out a plan of assay for kola especially intended to avoid these and some other common sources of error; it has been used by us in all the assays reported herein and in many others, and has given uniform and concordant results, higher than any we have yet seen. We offer it with a confidence based on experience.

Volumetric Method for Caffein Determination.—Before giving the details of manipulation for assay, it may be well to describe

[1] Kilmer, 1896: *Am. J. Pharm.*, 68. 104.

the volumetric method for the estimation of caffein which is substituted for gravimetric methods.

This new process, given by Gomberg[1] is based upon the very complete precipitation of caffein by Wagner's reagent from aqueous solutions when these are acidulated with mineral acids —a fact which seems to have been pretty generally overlooked by the text-books bearing upon the subject. This oversight is, no doubt, traceable to the fact that caffein, being soluble in water, with neutral reaction, and not forming salts permanent in water, is taken as free alkaloid for all tests in the wet way. Other alkaloids, for the most part, are taken in their salts, for reactions in solutions, their salts having the neutral reaction. Therefore the Wagner's reagent, like other reagents, was generally applied to the caffein solution without the presence of any acid, and under such conditions, it is true, as stated in the text-books, that "caffein is not precipitated by Wagner's reagent."

Gomberg recently investigated the subject at considerable length. Without entering into discussion of other features of his work, it may be stated briefly that he found that an aqueous solution of caffein, even so dilute as 1 to 8000, is precipitated by Wagner's reagent in the presence of mineral acid, and that the precipitate formed is constant in composition ($C_8H_{10}N_4O_2HI.I_4$) in varying conditions of formation.[2] Having established these facts, practical application of them was made for the volumetric estimation of caffein. A short outline of the principal features of this method follows.

A definite volume of Wagner's reagent of known strength is added in excess to the measured caffein solution slightly acidulated with sulphuric or hydrochloric acid, and the clear liquid is decanted off after the precipitate has settled or is filtered through asbestos after five minutes' standing. The excess of iodine is titrated with decinormal sodium thiosulphate solution, using an aliquot portion of the filtrate. From this the number of cubic centimeters of decinormal Wagner's reagent can be calculated, which number multiplied by 0.00485 equals the weight of the anhydrous caffein.

We have had considerable experience with this process for

[1] This Journal, 18, 331.
[2] This Journal, 18, 350.

estimating caffein, as one of us (K.) furnished the original analytical data for Dr. Gomberg's paper, and we have employed it almost exclusively in the work upon the caffein compound since that time.

The table of results (p. 71) is reproduced from Gomberg's article. By way of explanation it may be said that solutions of caffein of respectively 0.25, 0.50, 0.75, and 1.00 per cent. strength were used, the acidulation was with sulphuric acid, and Wagner's reagent was employed in varying proportions, using a very slight excess over the theoretical amount, one and one-third times the theoretical amount, twice the theoretical amount, and one-half the theoretical amount. The results show that the method accounts very accurately for the caffein, especially when the iodine solution is in considerable excess.

In Table No. 2 are given the results obtained where a considerable excess, eight to ten per cent., of sulphuric acid is used. The results are not very uniform and show that slight acidulation gives greater accuracy in the estimation.

The manipulations used by us are as follows: The caffein to be estimated is dissolved in water, acidulated with sulphuric or hydrochloric acid (preferably the latter[1]), avoiding an excess, and made up to a definite volume. The acid strength of this volume should be about one per cent. If the quantity of solution is not large, *i. e.*, not more than forty or fifty cc. the whole is taken; if large an aliquot portion is measured from a burette. Standard Wagner's reagent is run in from a burette, ten cc. at a time, shaking the solution after each addition and allowing it to stand a few moments so that the color of the supernatant liquid may be observed. When this liquid becomes wine-red the iodine solution is in sufficient excess, and the volume of Wagner's reagent added is read, at the same time noting the total volume of the mixed solutions. The caffein periodide is filtered out, after five minutes standing, with a dry asbestos filter, the filtrate collected in a clean dry vessel and transferred to the same clean and dry burette from which the caffein solution first, and later the iodine solution, were measured. (If calibrated burettes are used it is, of course, not necessary to employ the same one each time.)

[1] Caffein solution, 1 to 10000, acidulated by hydrochloric acid, is precipitated by Wagner's reagent, while 1 to 8000 is the limit if sulphuric acid be used.

TABLE NO. I.

Wagner's reagent employed.	I. Solution containing 0.25 per cent. of caffein.			II. Solution containing 0.50 per cent. of caffein.			III. Solution containing 0.75 per cent. of caffein.			IV. Solution containing 1.00 per cent. of caffein.			V. Solution containing 0.50 per cent. of caffein.		
	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.
Theoretical quantity plus 2 cc. ..	0.0600	0.0591 0.0589	98.33	0.1200	0.1175 0.1175	97.82	0.1500	0.1481 0.1471	98.40	0.1200	0.1182 0.1179	98.38	0.1200	0.1154 0.1165	96.78
1½ times the theoretical quantity	0.0750	0.0749 0.0749	99.88	0.1200	0.1191 0.1189	99 17	0.1500	0.1489 0.1485	99.13	0.1200	0.1191 0.1187	99.12	0.1200	0.1196 0.1197	99.75
Twice the theoretical quantity.....	0.0500	0.0502 0.0506	100.80	0.0800	0.0805 0.0789	99.63	0.1200	0.1184	98.67	0.1100	0.1091 0.1091	99.18	0.0800	0.0802 0.0791	99.63
One-half of the theoretical quantity.....	0.0750	0.0363 0.0363	48.40	0.1600	0.0794 0.0794	49.62	0.2250	0.1107	49.20	0.2000	0.1067 0.1067	53.35	0.1600	0.0791 0.0791	49.44

Columns I, II, III, and IV show the results obtained by decanting the clear liquid after the solutions had stood for one hour. In column V the results are those obtained by filtering the solution for titration through asbestos after five minutes standing.

TABLE NO. 2.

Wagner's reagent employed.	Caffein solution 0.25 per cent.			Caffein solution 0.50 per cent.		
	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.
Theoretical quantity + 2 cc.....	0.0500	0.0487 0.0492	97.90	0.0500	0.0468 0.0479	94.70
One and one-third times the theoretical quantity	0.0200	0.0204 0.0198	100.50	0.0675	0.0642 0.0639	94.89
Theoretical quantity × 2.....	0.0250	0.0251 0.0245	99.20	0.0500	0.0480 0.0490	97.00
One-half of the theoretical quantity	0.0250	0.0119 0.0128	49.40	0.0600	0.0275 0.0281	46.33

From this an aliquot portion is measured into a porcelain dish and exactly neutralized with tenth-normal sodium thiosulphate. Each cc. of Wagner's reagent consumed = 0.00485 of caffein. The following example will illustrate the method of calculation:

"Unknown" caffein solution 30 cc.+ 30 cc. Wagner's reagent = 60 cc.

30 cc. filtrate = 6.2 sodium thiosulphate solution.

Whole solution (60 cc.) containing 30 cc. Wagner's reagent= 12.4 sodium thiosulphate solution.

30 cc. Wagner's reagent—12.4 cc. thiosulphate = 17.6 consumed by caffein.

17.6 cc. Wagner's reagent × 0.0485 = 0.08536 caffein.

The asbestos filters described are conveniently prepared by placing a small perforated platinum disk in a medium sized carbon tube; on this a layer of glass wool one-fourth of an inch in depth is placed. By aid of a good filter pump, finely divided asbestos pulp, previously acid-washed and suspended in water, is deposited in thin layers by pouring on in small portions and applying suction. This is continued until a layer of asbestos three-fourths to an inch in height is obtained. By keeping the asbestos mixture well stirred during the first part of the operation and allowing it to settle during the latter, the coarser particles will be deposited in the lower layers and the finer ones on the top. The filter is now washed, successively, with hot water, alcohol, and ether, and after drying twenty minutes at 80–100° C., is ready for use.

In the event that it is desired to decant the liquid for titration, instead of filtering, it is advisable to perform the precipitation in

a tall slender cylinder or test-tube on foot. After the precipitate has settled compactly, the end of a burette is immersed in the liquid to the desired depth, and the liquid drawn upward by means of suction produced by a rubber bulb fitted to the top of the burette.

The precaution is always taken, of course, to have the caffein free from any other substance that will affect the iodine solution, and to perform the precipitation in cold solutions.

By the exercise of ordinary care and judgment this method for the estimation of caffein will be found extremely accurate and satisfactory, while with a small amount of practice it admits of very rapid work. Having used it in more than one hundred estimations recently we feel qualified to recommend it.

MANIPULATIONS IN THE ASSAY OF KOLA.

Preparation of Sample.—Slice a sufficient quantity of the fresh seeds in thin papery slices, allowing them to fall in a beaker of boiling alcohol.[1] An ordinary potato slicer is a very convenient and effective instrument for this purpose. Remove the slices after a few moments' boiling, and allow them to dry spontaneously on clean glass plates. Distil the alcoholic solution, under reduced pressure,[2] to a syrupy consistence, and pour it on the sliced drug now being dried, rinsing the flask with successive small portions of alcohol. When dry remove the drug to a mortar, wash the glass plates with a few cc. of hot alcohol, and pour this on the drug which is to be finely powdered and preserved in dry, glass-stoppered jars. The powder prepared in this way corresponds closely to the original color of the seeds, being but slightly paler in each instance. There can hardly be any doubt that it represents correctly the fresh seeds, with subtraction of the water, and perhaps of a portion of the trifling amount of volatile oil they contain.

For free Alkaloids.—Weigh accurately five grams of the sample, transfer to a Soxhlet's extraction tube, and treat for six

[1] The boiling alcohol kills the ferment and also dries the drug quickly. While it will appear later that this ferment, contrary to the general opinion, has but little if any influence on the production of free caffein from the caffein compound, the use of alcohol has nevertheless been retained as an efficient drying agent, and one that preserves the drug apparently without allowing any chemical change whatever to take place.

[2] The object being to avoid the decomposition of the caffein-bearing combination by the hot water remaining after the alcohol is evaporated.

hours, or until exhaustion is complete, with chloroform. Evaporate the chloroform, and to the residue add thirty cc. of hot, one per cent. hydrochloric acid, and filter to remove fat, rinsing out the flask with several small portions of hot water, passing these through the filter, and washing the filter three or four times with hot water. The united filtrate and washings now amount to about seventy to seventy-five cc. Concentrate in a porcelain capsule on a water-bath to about ten or fifteen cc., transfer to a graduated cylinder, which has been carefully compared with the burette to be used for the Wagner's reagent, and rinse the capsule with three or four successive portions of hot water, making up the volume in the cylinder to thirty cc. after cooling. Now run in from the burette thirty cc. standard Wagner's reagent, and agitate well. Filter through asbestos after five minutes, and pour the filtrate into the same burette, previously washed and dried. About fifty-five cc. will be recovered. Run out an aliquot portion of the liquid (say thirty cc.), and neutralize the excess of iodine with decinormal sodium thiosulphate solution, then from the result calculate the number of cc. of iodine solution consumed. Multiply this number by 0.00485 to obtain the weight of the anhydrous caffein. With another aliquot portion of the filtrate make a duplicate titration.

It will be observed that the alkaloids are estimated only as caffein. Theobromin also is precipitated by Wagner's reagent but its proportion, 1.48 to 100.00 of total alkaloids, is so small that the error introduced by the difference in the factors of the alkaloids is not appreciable.

The Combined Alkaloids.—After the exhaustion with chloroform add alcohol of ninety per cent. to the drug, which is still contained in the extraction tube, and continue the treatment until exhaustion is complete, as shown by the absence of color in the portion of menstruum last siphoned over in the apparatus. Two or three hours are usually sufficient. This alcoholic solution may be treated in either of the following ways:

(*a*) Evaporate the solution to dryness in a tared porcelain capsule, and weigh. Take a small portion (0.200 or 0.300 gram), and determine the amount of nitrogen by combustion. This nitrogen is entirely alkaloidal, as proteid substances are not

extracted from the drug by the strong alcohol, and the total nitrogen can be calculated into caffein. From the amount of caffein found by combustion of the aliquot portion, calculate the total amount present in the whole extract.

(*b*) To the hot alcoholic solution add an excess of freshly precipitated lead hydroxide (litharge or lead carbonate will not answer), and digest on a water-bath for a few minutes, until the supernatant liquid is colorless. Then transfer to a porcelain capsule, rinse the flask with hot alcohol, mix with clean white sand, evaporate the mixture to dryness, and place the whole in the extraction tube. Treat with chloroform three or four hours, and determine the caffein volumetrically as previously directed.

We present herewith a table showing the results we have obtained by this plan of assay :

The sample.	Moisture, per cent.	Duplicates.	Fresh kola.			Dried kola.		
			Free alkaloids. Per cent.	Combined alkaloids. Per cent.	Total.	Free alkaloids. Per cent.	Combined alkaloids. Per cent.	Total.
No. 1. Dried kola. (Mixed.)	6.16	I.				1.859	1.783	3.642
		II.				1.828	1.836	3.664
		Av'ge.				1.843	1.809	3.652
						Calculated for "dry."		
No. 2. Fresh kola, red and white seeds.	53.9	I.	0.512	0.927	1.439	1.111	2.011	3.121
		II.	0.556	0.841	1.397	1.206	1.834	3.040
		Av'ge.	0.534	0.884	1.418	1.158	1.922	3.080
No. 3. Fresh kola, red and white seeds, very moldy.	53.9	I.	0.590	0.815	1.405	1.280	1.770	3.050
		II.	0.548	0.893	1.438	1.190	1.938	3.128
		Av'ge.	0.569	0.854	1.423	1.235	1.854	3.089
No. 4. Fresh kola, white seeds.	51.2	I.	0.595	1.029	1.624	1.220	2.110	3.330
		II.	0.562	1.006	1.568	1.153	2.060	3.213
		Av'ge.	0.578	1.018	1.596	1.186	2.085	3.271
No. 5. Fresh kola, red seeds.	57.3	I.	0.503	0.687	1.190	1.180	1.610	2.790
		II.	0.452	0.700	1.152	1.060	1.640	2.700
		Av'ge.	0.478	0.693	1.171	1.120	1.625	2.745

In explanation of the foregoing results, it should be stated that sample No. 1 is not of the same lot of drugs as the other four, but is one that was analyzed in this laboratory last year, and is also African kola obtained then from the house of Frederick Stearns & Co.

In order to facilitate comparison of the fresh and dry drug, the percentages of alkaloids obtained from the fresh have been also calculated for the corresponding amount of dry kola.

These results are much higher than those usually seen, the main difference being that our method accounts for both free and combined alkaloids. It will be seen that about one-half of the total alkaloids of dry kola exist in combination, and in the fresh seeds more than sixty per cent. of the alkaloids are "combined." It should also be noted that so far as the yield of alkaloids is concerned, the moldy kola does not differ from that in perfect preservation. Furthermore there is a difference between the red and the white seeds, as shown by the percentage of alkaloids and moisture.

Method of Dohme and Engelhardt.—Dohme and Engelhardt[1] have examined the method employed by Schlotterbeck and Knox[2] and have proposed another one in its stead which has in their hands, given higher results. Their process requires to boil the dried and powdered drug in thirty per cent. alcohol for two hours, filter, evaporate the filtrate to dryness with sand and magnesia and exhaust this residue with chloroform. The residue left after evaporation of the chloroform is dried at 100° C., and weighed as caffein. Using this method they have obtained 2.10 per cent. of caffein from African kola.

We have given their method a careful trial with the gravimetric results stated next below, the sample used being No. 1 of the foregoing table:

I. 2.04 per cent.
II. 1.93 " "

Sources of Error.—That the caffein thus obtained, although apparently pure, is not so in reality, is shown by the fact that when titrated with Wagner's reagent the per cent. is much lower.

I. 1.76 per cent.
II. 1.68 " "

There are still other objections to the method. The treatment with thirty per cent. alcohol does not remove all the free alkaloids, for the drug under assay after having been boiled with the alcohol and washed, as directed, was dried and treated with

[1] *Am. Drugg.*, 1896, p. 12.
[2] *Proc. Am. Pharm. Ass.*, 1895, p. 334.

chloroform in an extraction apparatus. The residue left after evaporation of the chloroform gave positive test for caffein. Nor does the diluted alcohol remove all the combined alkaloids, for after the treatment with chloroform just described, strong alcohol was added to the drug in the extraction tube, and the extraction continued. The wine-red solution obtained was treated with an excess of lead hydroxide, filtered, and the clear colorless solution evaporated to dryness. This residue also contained caffein.

It appears that the combined alkaloids removed by the thirty per cent. alcohol in Dohme's process and treated with magnesia and sand are not completely liberated by this treatment, and consequently are not removed by the chloroform. For after this magnesia-sand residue had been exhausted by chloroform as directed, strong alcohol was used as a menstruum, and it removed another portion of combined caffein, identified by the lead hydroxide treatment above mentioned. In our hands, with careful manipulation, the greatest amount of actual caffein obtained by this method is a little less than one-half of the total amount present, as shown by assay after the process described in this article.

Thanks are due to Mr. Robert J. Nisbet, Ph.C., for valuable assistance rendered in the assays and in the analyses by combustion.

GLUCOSIDE OF KOLA.

In the literature of kola is found frequent mention of a glucoside yielding caffein, glucose, and "kola red" on decomposition.[1] It has been stated that this glucoside is an extremely unstable body; that heat, moisture, dilute acids,[2] the ferment[3] of kola, or diastase is sufficient to re-solve it, partly or wholly, into its component parts.

It has even been suggested[4] that no alkaloids exist free in the fresh seeds, but they are wholly combined in this glucoside.

Methods for Separation.—The process used by Hilger,[5] and later by Schweitzer[6] for the isolation of this so-called glucoside, "kolanin," is as follows:

[1] E. Knebel, 1892: *Apoth. Ztg.*, **7**, 112.
[2] A. Hilger, 1893: Dtsch. Vierteljahres. für Offent. Geshtspfl., **25**, 559.
[3] C. Schweitzer, 1895: Inaugural-Dissertation, Munich.
[4] Knebel: *Loc. cit.*
[5] *Loc. cit.*
[6] See Schweitzer, 1895: Inaugural-Dissertation, Munich.

The drug is exhausted with alcohol, the extract evaporated to dryness, and the residue washed with water; then the insoluble portion is dissolved in weak alkali solution. To this, dilute mineral acid is added in slight excess, when the "kolanin" is precipitated. It is collected by filtration, washed with water, and dried. It is a red brown amorphous powder, containing 0.9 per cent. of ash. We have prepared a number of specimens from both the fresh and dried drug, by this process which we shall call Method No. 1. For purposes of comparison we have also employed other processes. In one of these, Method II,[1] the portion of alcoholic extract insoluble in water is dissolved in strong alcohol, and this solution then precipitated by the addition of about three volumes of ether. The precipitate is rapidly filtered at the pump, washed with ether, and dried in a vacuum desiccator over sulphuric acid. The product is a light impalpable powder, cream to light red in color, and is ash-free after three precipitations.

By another method (III) the residue left after washing the alcoholic extract with water was dried in a vacuum desiccator, powdered, and treated with chloroform to remove fat and whatever free alkaloids the water washing had left behind. Again dried and powdered, it furnished a product appearing much like that of Method I, but somewhat lighter colored.

We present herewith (p. 79) a table of results obtained by combustions of samples prepared from both the fresh and the dry seeds by the methods just described.

We do not at present enter upon interpretation of the above results for carbon, hydrogen, and nitrogen,[2] but leave their study until further work on this body, as now planned, shall have been finished. It seems to be largely a question of structure, and this must be settled before it can be positively stated whether the caffein compound in kola is a glucosidal body, or only a glucoside-bearing body. And, of these, the one may not differ from the other except in the order of its stages of decomposition. There is much evidence tending to show that this so-called glu-

[1] In Methods II and III, all distillations are carried on under reduced pressure.

[2] Following are the figures, respectively, of Schweitzer and of Hilger, for the cacao glucoside, the former by calculation from the yield of alkaloids and glucose, the latter by analysis (*Deutsch. Vierteljahr. Oeffentl. Gesundh.*, 1893, **25**, 559.)

GLUCOSIDE OF KOLA.

	Calculated.		Found.											
			Method I.				Method II.				Method III.			
			From dry seeds.		From fresh seeds.		From dry seeds.		From fresh seeds.		From dry seeds.		From fresh seeds.	
Duplicates.	By Knebel :[1] $C_{14}H_{13}(OH)_5 + C_6H_{12}O_6 + C_8H_{10}O_2N_4$.	By Schweitzer :[2] $C_{40}H_{56}N_4O_{21}$.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
C	52.50	51.71	62.11	61.91	61.82	61.70	61.39	61.71	62.16	61.96	62.06	62.22	61.43	61.26
H	6.25	6.03	7.06	7.12	6.98	7.16	6.62	6.79	7.05	7.16	6.80	6.96	6.87	6.98
N	8.75	6.03	8.04	7.74	6.04	5.97	5.89	5.67	6.23	5.95	6.92	6.74	6.13	5.94
O	32.50	36.23	22.79	23.23	25.16	25.17	26.10	25.83	24.56	24.93	24.22	24.08	25.57	25.82
Caffein by calculation from the N	30.31	20.88	27.85	26.81	20.92	20.68	20.40	19.64	21.58	20.61	23.97	23.34	21.23	20.57

[1] Assumed from the proportions of free caffein and glucose found in dry kola.

[2] Assumed from the respective yields of alkaloids and glucose by hydrolysis of the glucoside.

	Cacao glucoside.	
	Calc. by Schweitzer: $C_{80}H_{86}O_{15}N_4$.	Found by Hilger: $C_{68}H_{86}O_{36}N_4$.
C	65.34	52.85
H	7.80	6.22
N	5.08	3.63
O	21.78	37.30

coside is in reality a mixture of tannates of caffein and theobromin, and that the glucose obtained on hydrolysis is split off from the tannin. These evidences are given a little later on in this paper.

After combustion, the next step was to ascertain, if possible, whether the nitrogen was wholly that of the alkaloids or not.

ACTION OF DILUTE ACIDS.

It was attempted to recover the caffein, quantitatively, and for this purpose hydrolysis with dilute mineral acids was first resorted to.

Following carefully the methods of Schweitzer, *viz.*, to boil the "glucoside" for from four to six hours with twenty times its weight of five per cent. sulphuric acid, filter, neutralize the filtrate with barium carbonate, filter again, and estimate the caffein and glucose in the clear filtrate made up to a definite volume, we are unable to obtain results concordant with his. The method was also varied to admit of the removal of the dissolved tannin which remains in the clear filtrate after neutralization with barium carbonate, by precipitating it as lead tannate, filtering, removing excess of lead salt with hydrogen sulphide and boiling off the latter.

The strength of the acid used was varied from two to twenty per cent. and the time of boiling from two to ten hours. But in no case was the amount of caffein recovered equal to that indicated by the nitrogen percentage. In the samples used, the calculated proportion of caffein was, in round numbers, from 21.00 per cent. to 24.00 per cent. Yet 15.00 per cent. was the greatest

amount recovered, and the other amounts varied from that down to 4.76 per cent., the lowest.[1]

Hydrochloric acid diluted to the same strength was next tried with somewhat better but very unsatisfactory results.

It was now in order to institute a control analysis to determine whether or not all the caffein could be recovered after such treatment as has been described. To this end an experiment was made, as follows:

Duplicate samples of 0.300 gram pure caffein, and 0.500 gram pure kola tannin were boiled together with thirty cc. five per cent. sulphuric acid, after which the caffein was estimated in the way above described.

I. Taken 0.300. Recovered, 0.2635. Loss, 12.17 per cent.
II. " 0.300. " 0.2541. " 15.30 "

This loss suggested the possibility that some of the caffein might have combined with the tannin. Accordingly the reddish residue filtered out after boiling with acid was dried and exhausted with chloroform to remove all traces of free caffein. Then boiling alcohol was used as a menstruum, and gave a wine-red solution which was treated with lead hydroxide. The clear filtrate on evaporation gave positive evidence of caffein, both by appearance of the crystals and by chemical tests, showing that caffein tannate is actually *formed* during this process of treatment. Now if this is the case, it is hardly to be expected that the so-called "kolanin," a body very similar in properties to caffein tannate, would be quantitatively *decomposed* under exactly the same conditions. Indeed the experiments already described have shown that it is not. Nor is the statement[2] borne out that twenty per cent. sulphuric acid decomposes this natural combination of caffein completely, as the experiment described next below demonstrates.

[1] In this case the extremely low result is to be attributed in part to decomposition of the caffein in the course of the analysis. The tannin dissolved was removed in the way recommended by the United States Department of Agriculture, Division of Chemistry, Bulletin 46, p. 72, *i. e.*, by precipitation with lead acetate, and removal of excess of lead from the filtered liquid by the addition of sodium carbonate. The low result suggested the possibility of the decomposition of caffein by the solution of alkali carbonate, it being well known that alkali hydroxide solutions effect a decomposition into caffeidin, etc., on heating. So an experiment with a known quantity of pure caffein was tried: 0.110 gram caffein was boiled with ten per cent. sodium carbonate solution for four hours; and the caffein estimated volumetrically, 0.0593 gram being recovered, a loss of 46.1 per cent.

[2] Kilmer, 1896: *Am. J. Pharm.*, 96.

1.250 grams of the so-called glucoside were boiled vigorously with forty cc. of twenty per cent. sulphuric acid, and then filtered. The insoluble residue was examined in the way described in the preceding experiment, and "kolanin," apparently unchanged, was found, the evidence being quite positive.

Furthermore, it is not improbable that the hydrolysis of this substance is attended with incomplete recovery of the alkaloid liberated, for the four filtrations necessary, *viz.*, for removal successively of the insoluble red residue, barium sulphate, lead tannate, and lead sulphide are very likely to be accompanied by a loss of caffein from its adhesion to the moist, bulky precipitates.

Hydrolysis with dilute acids having been shown to be unsuited for the purpose of recovering completely the alkaloids from their natural combination, other and entirely different means were resorted to.

ACTION OF LEAD HYDROXIDE.

Recalling the fact that this so-called glucoside bears a close resemblance in properties to alkaloidal tannates, and in view of the action of lead hydroxide on this class of bodies, it was decided to try its effect upon "kolanin." Qualitative experiments to this end proving successful, it was next in order to ascertain whether or not the liberation of caffein was quantitative, and a full recovery possible. For this purpose 0.500 gram of the so-called "kolanin," whose average nitrogen content indicated 0.1052 gram caffein, was dissolved in twenty-five cc. hot ninety per cent. alcohol. To this, freshly precipitated lead hydroxide previously triturated with hot alcohol to a smooth cream was added, until, after a few moments' standing to allow subsidence of the precipitate, the liquid was clear and colorless. The mixture was then evaporated to dryness on a water bath, clean dry sand added to give the requisite volume, the whole then transferred to a Soxhlet's tube, and the beaker carefully rinsed with chloroform, the rinsings being added to the contents of the tube. Chloroform was then added, and extraction continued for two hours. The chloroform solution was then evaporated, and the caffein estimated volumetrically, 0.1040 gram being recovered.

This treatment does not decompose caffein, for 0.200 gram pure caffein dissolved in alcohol with 0.500 gram pure kola-

tannin and treated as above described yielded 0.1991 gram on volumetric estimation.

This simple and rapid process for liberating the caffein from the caffein compound affords a means for a very accurate determination of the combined alkaloids of kola, of which fact use has been made in the method of assay proposed and used by us, as previously described.

This reaction of kolanin with lead hydroxide indicates a tannate-like character for the body. There is reason to think that the glucose obtained by decomposing this so-called glucoside with mineral acids exists primarily in combination with the tannin-like body, for after chloroform had removed all the caffein from the mixture of alkaloids, lead salt, lead hydroxide and sand, described above in the experiments with "kolanin," treatment with water removed nothing further. The liberation of glucose therefore is not necessarily simultaneous with that of caffein, nor in consequence of it. This was further shown by decomposing the lead salt formed by the red coloring matter, through treatment with hydrogen sulphide, and thereby recovering the colored body previously combined with the caffein. This body so obtained, gives all tannin reactions toward iron salts, alkaloids, gelatin, etc., and has a pronounced astringent taste. On treating it with dilute mineral acid, in the manner directed by text-books,[1] very positive evidence of glucose was given, not only by its behavior with Fehling's solution, but with phenylhydrazin as well, of which mention is made later. The foregoing facts would seem to indicate that the so-called glucoside is a combination of caffein (and theobromin) with a glucoside tannin.

ARTIFICIAL KOLA-TANNATE OF CAFFEIN. METHOD OF PREPARATION.

By way of further investigation into this question we undertook to prepare artificially from kola-tannin and pure caffein a similar product which we proposed to compare with the natural compound. This was successfully accomplished as follows: An aqueous infusion of kola is poured into a ten per cent. solution of caffein acidulated with hydrochloric acid. The presence of

[1] Prescott: Organic Analysis, 467.

acid is necessary to obtain an aqueous caffein solution of sufficient concentration, and especially to avoid the re-solution of the tannate of caffein which takes place in the neutral solutions in the presence of an excess of either tannin or caffein. The precipitate, abundantly formed, is rapidly filtered at the pump, washed with cold water, and well drained. It is then dissolved in alcohol, and filtered to remove insoluble extraneous matter carried down in precipitation. The alcohol is then distilled off under reduced pressure until the solution has reached a syrupy consistence, and the evaporation continued to dryness over sulphuric acid in a vacuum desiccator.

PROPERTIES OF KOLANIN AND CAFFEIN KOLA-TANNATE COMPARED.

The product obtained is identical in appearance and sensible properties with the so-called kolanin. Both are insoluble in water, ether, chloroform, and cold dilute mineral acids; freely soluble in alcohol with dark wine color, from which solution they are re-precipitated by two or three volumes of ether; soluble in dilute acetic acid, more easily on warming; sparingly soluble in warm acetone; soluble in warm neutral caffein solution, and in warm kola-tannin solution; quite soluble in dilute alkali (both fixed and volatile) solution[1] with production of a very dark color, and at once reprecipitated therefrom by dilute mineral acids in slight excess, also by acetic acid, though the precipitate redissolves in an excess of the acetic acid on warming. They are decomposed in alcoholic solution by lead acetate and lead hydroxide. In all the ways tried both deport themselves alike and in a manner not inconsistent with the chemical behavior of an alkaloidal tannate.

Pure kola-tannin was also used for the preparation of the caffein salt, and yields a product identical in appearance and properties with that prepared from the impure kola-tannin of aqueous infusion of kola. But as the compound of the pure tannin does not apparently differ from the precipitate of caffein with kola infusion, the latter, less difficult of preparation, has been em-

[1] Considerable caffein may be removed from this alkaline solution by shaking out with chloroform. It is possible that the tannate is decomposed in part or wholly by the alkali and reformed upon addition of acid. The process is wasteful, so it is likely that the re-formation, if it occurs in this way, is complete.

ployed in the preparation of the several samples of caffein kola-tannate used for determining elementary composition, namely:

I. Prepared as described above. Reddish-brown powder, with astringent and bitterish taste.

II. In same way as Number I, the final product being dissolved in dilute alkali solution, and reprecipitated by dilute hydrochloric acid, filtered, washed, and dried. Reddish-brown powder, with astringent and bitterish taste.

III. In the same way as Number I, except that the final product was dissolved in alcohol and precipitated by ether, filtered, washed with ether, and dried. Lighter in color, but similar in taste to Number I.

IV. The clear filtrate after the precipitation of Number I gave, on twenty-four hours' standing, another copious precipitation of caffein kola-tannate, which was recovered in the usual way. Appearance and taste like that of Number I.

The following table shows the results obtained by duplicate combustion of each of these samples for carbon, hydrogen, and nitrogen:

CAFFEIN KOLA-TANNATE—ARTIFICIAL.

	Found.							
Method.	I.		II.		III.		IV.	
Duplicates.	1.	2.	1.	2.	1.	2.	1.	2.
C	59.27	59.41	60.11	59.89	59.64	59.35	59.94	60.22
H	6.21	6.02	6.18	6.07	5.96	6.10	6.08	6.24
N	6.20	5.96	5.30	5.54	5.61	5.45	5.15	5.27
O	28.32	28.61	28.41	28.50	28.79	29.10	28.83	28.27
Caffein calculated from the N	21.47	20.64	18.35	19.19	19.43	18.87	17.83	18.25

It will be seen by comparing these figures with those given for the natural form of combined caffein extracted from kola by physical solvents in our method, that the composition of the one does not differ very widely from that of the other, and that this artificial product has a fairly uniform and constant composition. It is, of course, a well-understood fact that the composition of alkaloidal tannates is by no means strictly constant, but that it varies according to temperature and concentration of solutions

used, and the mass of each used with respect to that of the other. The well-known variation in the composition of the same kind of tannin, obtained under different conditions, is also to be taken into account. The natural form of combined caffein, called kolanin, yields on an average about twenty-two per cent. of caffein, while that obtained artificially gives a slightly lower amount, about nineteen per cent. being the average. The difference may, perhaps, be due to the different conditions of formation, and not to any difference in the character of the bodies themselves. And, as previously stated, so far as reactions and physical properties are concerned, leaving a slight difference in elementary composition out of consideration, we have not thus far found any radical difference between the natural and the artificial products.

ACTION OF FERMENTS.

In order to ascertain whether or not diastase would liberate caffein from the so-called glucoside, the following test was made: 0.500 gram of the natural caffein compound of kola, and 0.0500 gram of pure diastase,[1] known to be 1 : 100, in twenty-five cc. distilled water, were kept at a temperature of 50°–53° for twenty-four hours, and for thirty-six hours at the ordinary temperature; the caffein liberated was then estimated. A control test was made at the same time, using the same amount of the caffein-bearing body, and the same volume of water, but no diastase. This was kept under exactly the same conditions of temperature and time as the first, and the caffein then estimated.

Sample with diastase yielded 0.0689 caffein, equal to 56.50 per cent. of the whole amount present.

Sample without diastase yielded 0.0706 caffein, corresponding to 58.83 per cent. of the total amount present.

This experiment was repeated on the artificial caffein kola-tannate with similar results.

These results indicate that the liberation of caffein is not due to the diastase, but to the water and heat used for its exhibition.

It was next in order to learn, if possible, the influence of the ferment of kola on the liberation of caffein from its combination

[1] Prepared by Mr. D. L. Davoll, Jr., Instructor in Organic Chemistry in the School of Pharmacy of this University, to whom our thanks are due.

existing in kola. For this purpose several perfectly fresh and sound red and white seeds were selected. One-half of the number were sliced into sixty cc. of water and kept for sixteen hours at 50°–55° and for twenty-four hours at ordinary temperature, then evaporated to dryness, powdered, and the free caffein estimated in duplicates in a weighed portion. The other half of the seeds were similarly treated, except that the slices were received in boiling water to destroy the ferment; and the whole was then kept at 50°–55°, the same length of time as those described above, then evaporated to dryness, powdered, and assayed.

Sample.	Per cent. Caffein.[1]	
	I.	II.
Not sterilized	0.644	0.639
Sterilized	0.629	0.662

It would seem from the above stated results that the kola ferment does not assist in the liberation of caffein from its natural combination, but that such liberation as takes place is rather to be attributed to the presence of moisture and warmth.

Moreover, it is of significance respecting the caffein compound, to observe that sterilizing the kola, which checks the formation of the colored body called kola-red, does not at the same time check the liberation of the alkaloid. In other words, it does not at all appear that caffein and kola-red are joint products of the one hydrolysis of a glucoside, though such has been the conclusion of previous investigators.

ESTIMATION OF THEOBROMIN.

This alkaloid forms such a small proportion of the total alkaloids that it is usually ignored in an assay, the whole being computed as caffein. As its ratio to the caffein present seems to be pretty constant, there appears no particular objection to this procedure unless a very precise analysis is desired.

We have found the gravimetric method proposed by Kunze,[2] with a few modifications, very satisfactory for the estimation of theobromin in the presence of caffein.

[1] Calculated for fresh seeds.

[2] W. E. Kunze, 1894: *Ztschr. anal. Chem.*, 24.

It is, however, necessary to purify the alkaloids by recrystallizing twice from water, or the traces of tannin and coloring matter adhering will reduce the silver nitrate and lead to erroneous results. After purification and drying at 100° C., 0.500 gram of the alkaloids of kola is dissolved in twenty-five cc. water, a few drops of ammonia added, and then five cc. silver nitrate solution (reagent), and the liquid heated on a water bath until the ammonia is entirely expelled. The silver theobromin is precipitated, and collected on a weighed asbestos filter, and washed with hot water until the washings no longer show the presence of a silver salt by the addition of hydrochloric acid. Hot dilute hydrochloric acid is now passed through the filter, followed by hot water until the washings are free from all traces of hydrochloric acid. The silver chloride remaining in the filter is now washed successively with alcohol and ether, dried twenty minutes at 85°–100° C. and the tube weighed. From the weight of the silver chloride we have the proportion:

Molecular weight of AgCl: Molecular weight of $C_7H_8N_4O_2$: : Weight of AgCl : x = weight of the theobromin.

In total free alkaloids the proportion of theobromin was found to be 1.48 per cent., and in the total combined alkaloids, as would be expected, very nearly the same, in this case 1.51 per cent. Schweitzer,[1] however, found that it constituted 19.70 per cent. of the total combined alkaloids, and suggested that the increased amount of theobromin may be due to its formation from caffein by the prolonged boiling with the five per cent. sulphuric acid used by him for hydrolysis of the supposed glucoside.

But as a matter of fact, a methyl group is not so easily eliminated from caffein. That five per cent. sulphuric acid will not effect this change is shown by the results of the experiment next described. 0.3494 gram of caffein boiled for six hours with twenty-five cc. of five per cent. sulphuric acid showed at the end of that time not the slightest trace of theobromin by the silver nitrate test previously mentioned, and 0.3485 gram was recovered. Nor is caffein changed or colored by concentrated sulphuric acid even at 100° C.[2]

[1] 1895: Inaugural Dissertation, University Munich.

[2] Prescott's Organic Analysis, p. 82; Allen's Commercial Organic Analysis, vol. iii, pt. ii, 478.

Schmidt[1] found that by heating caffein with concentrated hydrochloric acid in a sealed tube for six to twelve hours, at 250° C., ammonia, sarcosin, methylamine, carbon dioxide, and traces of formic acid were formed, but no theobromin; he also found that concentrated hydrochloric acid has no action on caffein below 200°.

MELTING-POINT OF THE ALKALOIDS.

After repeated purification, the melting-point of the mixed free alkaloids of kola was taken, as was also that of the combined alkaloids; both were the same, 225°–227°, corresponding fairly well with that of pure caffein.

TANNIN.

(1) *Free Tannin.*—This was separated in various ways, the preferred method being as follows, taken in part from Allen:[2] The drug is exhausted with ninety-five per cent. alcohol, the alcoholic solution distilled *in vacuo* to a syrupy consistence, then washed with cold water. The insoluble matter is removed by decantation or filtration, and the clear wine-red solution fractionally precipitated with lead acetate (or lead hydroxide), the first and last portions of lead tannate being rejected. The lead tannate after being well washed is suspended in alcohol and decomposed with hydrogen sulphide. After filtration the alcoholic solution of tannin is distilled *in vacuo* to syrupy consistence and evaporation finished in a vacuum desiccator over sulphuric acid.

The tannin thus obtained is light-red to red-brown, having a faintly acidulous and decidedly astringent taste; deports itself as other tannins do towards iron salts ("iron greening"), gelatin, alkaloids, etc., etc. It is a glucosidal body, yielding on hydrolysis with mineral acids a dark-brown body. This was found to be insoluble in water or alcohol, and to give, on combustion, 69.20 per cent. of carbon, and 6.70 per cent. of hydrogen;[3] with the dark brown body was obtained glucose, identified by its action on Fehling's solution, and towards phenylhydrazin, with which latter it forms an osazone. We did not

[1] E. Schmidt: *Ann. Chem.* (Liebig), 217, 270.

[2] Allen's Commercial Organic Analysis, vol. iii, pt. i, p. 76.

[3] These figures do not correspond with those given by Knebel for kola red $C_{14}H_{13}(OH)_5$.

obtain a sufficient quantity of this osazone to take its melting-point, but its presence gave evidence of the glucosidal nature of the tannin.

(2) *Combined Tannin.*—The tannin existing in kola in combination with the caffein (as the so-called glucoside) was separated by means of lead hydroxide, following the above described manipulations. This "combined" tannin agrees in appearance and properties with the free tannin already described, being also a glucoside tannin.

The results obtained by combustion are also stated next below:

Duplicates.	Free tannin.		Combined tannin.	
	I.	II.	I.	II.
C.....	53.36	53.57	55.61	55.78
H.....	5.19	5.28	5.37	5.54
O.....	41.45	41.15	39.02	38.68

All calculations upon the composition of this body are reserved until after further work in its separation.

ANN ARBOR, MICH., JULY 6, 1896.

OBITUARY.

DR. HENRY A. MOTT, who has been an active member of the American Chemical Society since its organization in 1875, died at his home in New York City, on November 8, 1896. He was a grandson of the famous surgeon Dr. Valentine Mott, and was born at Clifton, Staten Island, New York, October 22, 1852. His primary education was obtained in the private schools of Rev. Mr. Tufts, at Munson, Mass., and of Prof. Berthet, on Broadway, near 18th street, in New York City. Later he entered the Academic Department of Columbia College, but finding the courses of study therein not wholly suited to his tastes and ambition, he applied for work leading to the degree of Doctor of Philosophy. On June 14, 1869, he entered the School of Mines in the course of mining engineering, and in 1873 he was graduated, receiving at the same time the degree of Bachelor of

Philosophy in metallurgy and Engineer of Mines in the course of engineering.

In pursuance of his studies in the School of Mines, he showed special aptitude for chemical work, and after his graduation, during the months of August and September, 1873, he served as private assistant to Dr. Charles F. Chandler in the laboratory of the School of Mines. In 1874 he was appointed chemist to the sugar refining firm of Havemeyer & Elder, in which capacity he served for seven years, or until 1881. While connected with the sugar refinery, and during 1875 and 1876, he was enrolled as a post-graduate student in Columbia College, and in the summer of the latter year, in consequence of the work prosecuted in this connection, he was awarded the degree of Doctor of Philosophy.

In 1881 he was elected Professor of Chemistry in the New York Medical College and Hospital for Women, and he continued in this professorship during five years. About this time he became identified with the manufacture of oleomargarine and artificial butter by the method of Megé-Mouries, and devised a process for preventing the crystallization of the product, so prejudicial to its commercial value.

His work now became directed to the study of foods and their adulteration and his activity in this particular led to his appointment to the office of Food Inspector of the Bureau of Indian Affairs under the United States Department of the Interior, in which he was called upon to make chemical examination of all food materials supplied by the government to the Indians.

His efforts were later directed to toxicological investigations and he was elected chemist to the New York Medico-Legal Society, to which he contributed many papers relating to the action of poisons in the animal system, their distribution in the cadaver and their detection in animal matter.

Among the well-known cases in which his services were engaged are the Belmont horses cases, in which the animals were poisoned with silver nitrate and corrosive sublimate, respectively; the celebrated Ben Ali or Shakespeare case, in which he was retained by the French Government for the defense; and the Fleming case, lately tried in New York City.

At the time of his death he was one of the lecturers in the

Free Lecture Course organized under the direction of the Board of Education of New York City, and he served actively in this connection during the six years immediately preceding his death. Among the subjects treated by him in course are, "Fire and the Methods of Extinguishing," "Light and Color," and "The Five Senses."

The more important of his chemical work is represented in the following titles from among his published books and papers:

"Milk of the African and Caucasian Races," 1876; "Artificial Butter," 1876; "The Scientific Manual," 1876; "The Chemist's Manual," 1877; revised in 1882; "The Adulteration of Milk," 1878; "Examination of Quinine," 1879; "Absorption of Sugar," 1879; "Alumina Salts on the Gastric Juice," 1879; "Alum Baking Powders," 1880; "The Megé Discovery—Oleomargarine Butter," 1880; "Oleomargarine and Oleomargarine Butter," 1880; "Memoirs on Oxygen," 1881; "Post-Mortem Imbibition of Poison," 1889; "Expert Testimony."

In 1886 the University of Florida conferred upon him the degree of Doctor of Laws.

In addition to his other literary work he published a book entitled "Yachts and Yachtsmen of America," and another discussing the question, "Was Man Created?"

Dr. Mott was most enthusiastic in the prosecution of any enterprise or investigation in which he became interested and his industry is shown in his published results. He was a genial companion and a faithful friend, and he will be missed from among the circle of his associates even as he is from his home. In his death the Society loses one of its useful members.

WM. MCMURTRIE.

BOOKS RECEIVED.

Chemistry for Engineers and Manufacturers. By Bertram Blount and A. G. Bloxam. Volume II. Chemistry of Manufacturing Processes. With illustrations. 484 pp. Philadelphia: J. B. Lippincott Co. London: Charles Griffin & Co., Ltd. 1896. Price $2.50.

Bulletin No. 44. Second Series. Charbon or Anthrax, with experiences during recent outbreak in North Louisiana. By S. B. Staples and W. H. Dalrymple. Baton Rouge: Louisiana State Experiment Station. 52 pp.